Polycyclic Aromatic Hydrocarbons (PAHs): Sources of Ambient Quinones:

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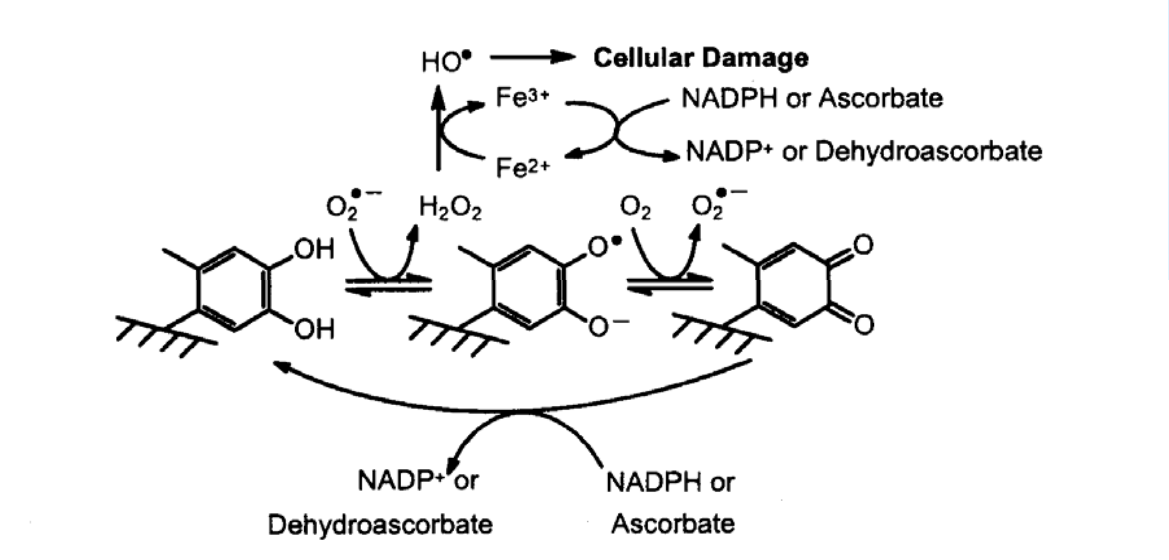
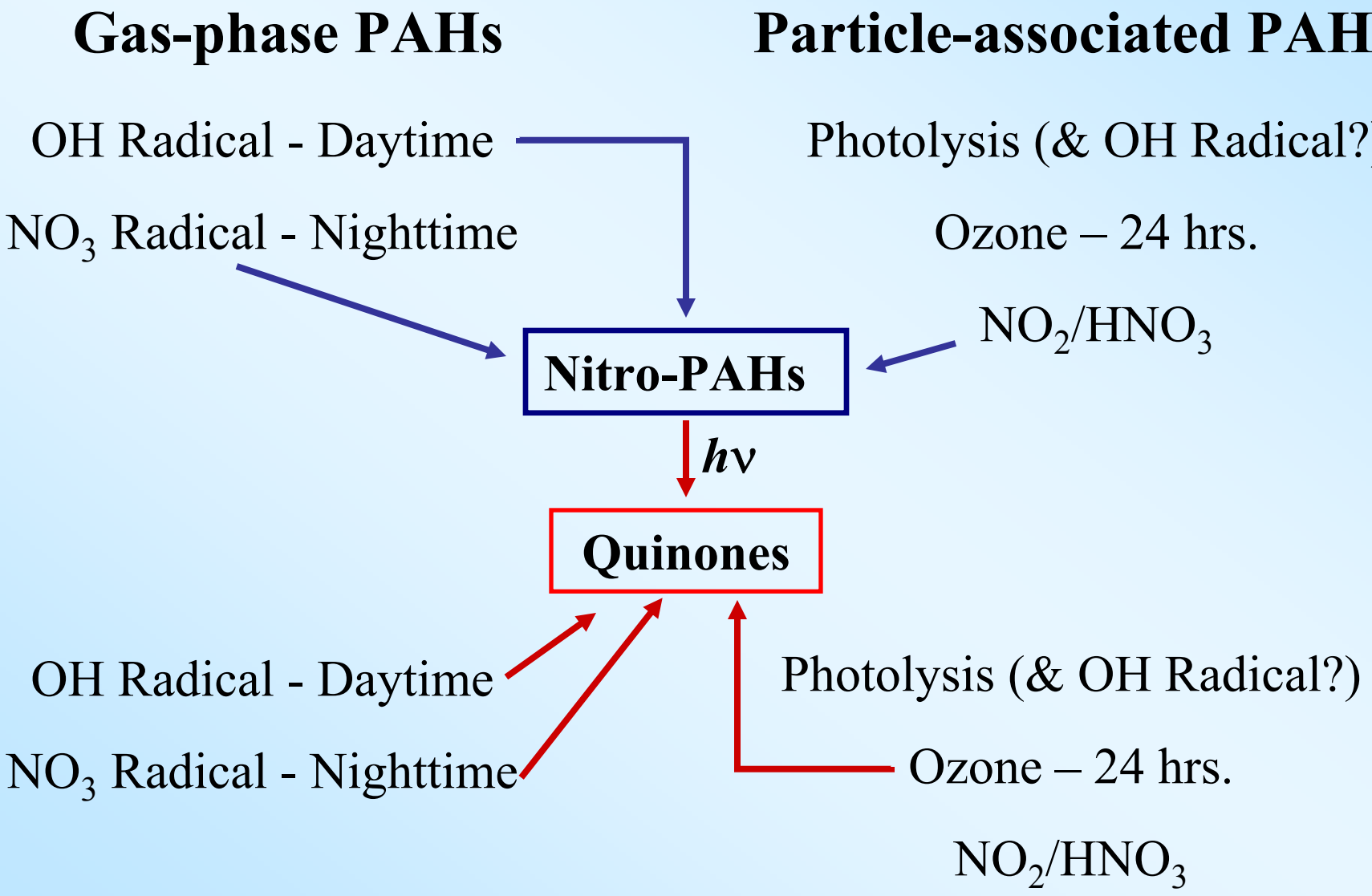
Potential Health Impacts of Ambient Quinones

- Quinones may covalently bind to proteins and/or DNA.
- Quinones may undergo redox cycling with their semiquinones, leading to formation of reactive oxygen species (ROS).

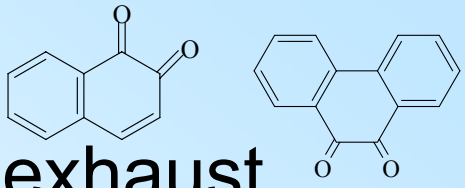


Squadrito et al., Free Radical Biol. & Medicine, **31**, 1136 (2001).

Atmospheric Formation of Nitro-PAHs & PAH-quinones



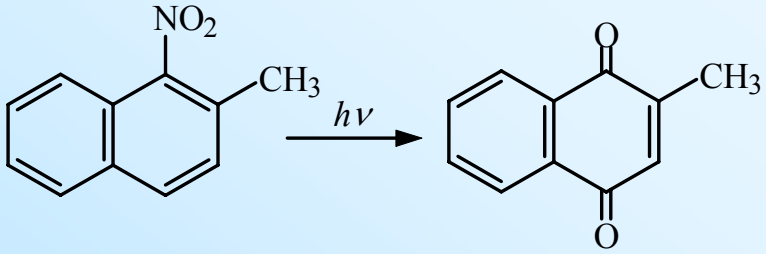
Sources of Ambient PAH-quinones



- Direct emissions, *e.g*. from diesel exhaust.

- Atmospheric formation from radical-initiated gas-phase reactions of PAHs.

- Photolysis of nitro-PAHs.

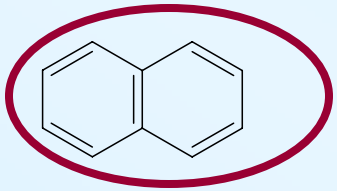


NO_3 + C_2-naphthalenes → dimethylnitronaphthalenes /ethylnitronaphthalenes

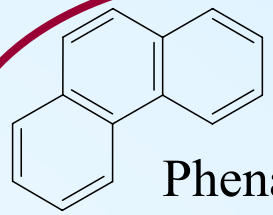
- Heterogeneous reactions of PAHs on particles, *e.g.* with ozone.

Jan. 2003, Los Angeles Reisen and Arey, ES&T (2005) 39, 64-73.

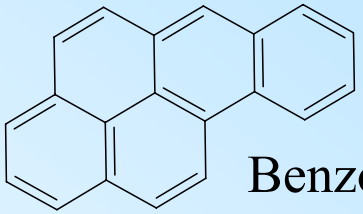
Gas-phase → Particle-associated



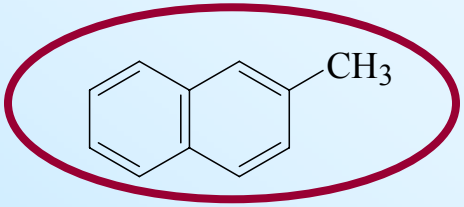
Naphthalene
0.08 Torr
1600 ng/m^3



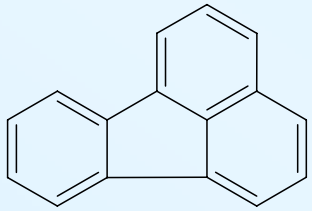
Phenanthrene
1.2 x 10^{-4} Torr
17 ng/m^3



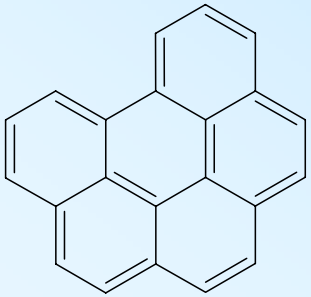
Benzo[a]pyrene
0.8 ng/m^3
*Fine et al.



2-MN 730 ng/m^3
Σ MNs 1000 ng/m^3

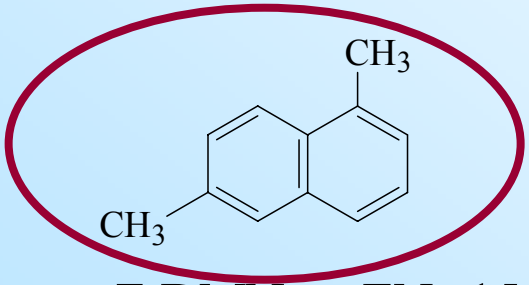


Fluoranthene
9.2 x 10^{-6} Torr
6.0 ng/m^3

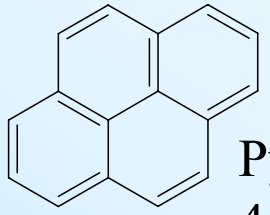


Benzo[ghi]perylene
1.9 ng/m^3

*Fine et al., ES&T (2004) 38, 1296-1304.



Σ DMNs + ENs 155 ng/m^3



Pyrene
4.5 x 10^{-6} Torr
6.9 ng/m^3

More abundant → Less abundant

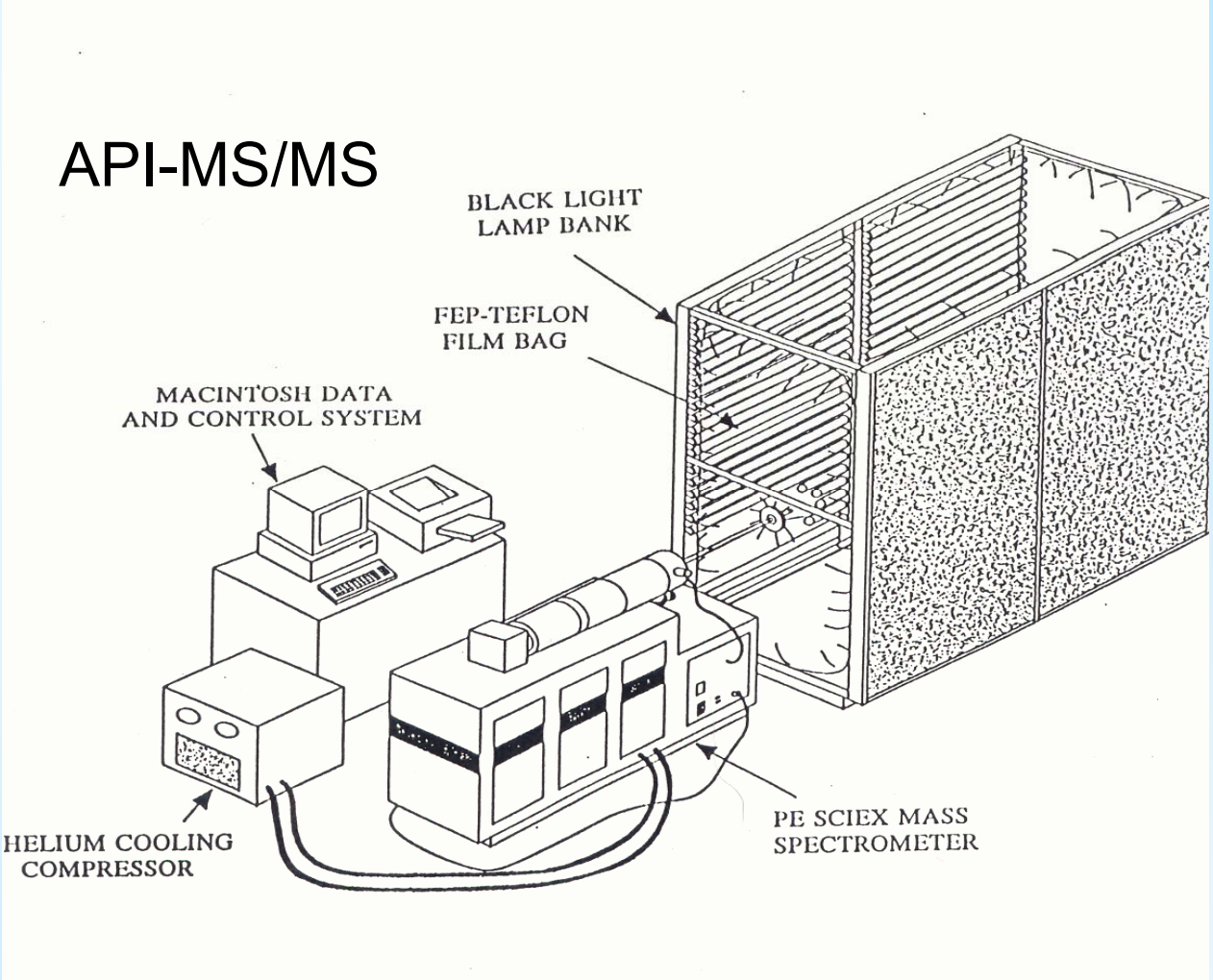
PROJECT OBJECTIVES

Evaluate the potential for atmospheric reactions to contribute to the atmospheric PAH-quinone burden by:

- Assessing formation of PAH-quinones from atmospheric reactions (OH, NO_3, O_3) of naphthalene, alkylnaphthalenes and phenanthrene.
- Identifying the dimethylnitronaphthalenes (DMNNs) formed from atmospheric reactions of selected dimethylnaphthalenes (DMNs) and studying their photolysis products, which were expected to include quinones.

Atmospheric Pressure Ionization-Mass Spectrometry for Product Identification

In-situ API-MS/MS: selective sensitivity, (excellent for screening for polar products). Protonated $[M+H]^+$ ions (separation of isomers may be possible by MS/MS, but requires standards to be available).



In-situ screening for quinones.

Product Identification

Gas Chromatography/Mass Spectrometry (GC/MS)

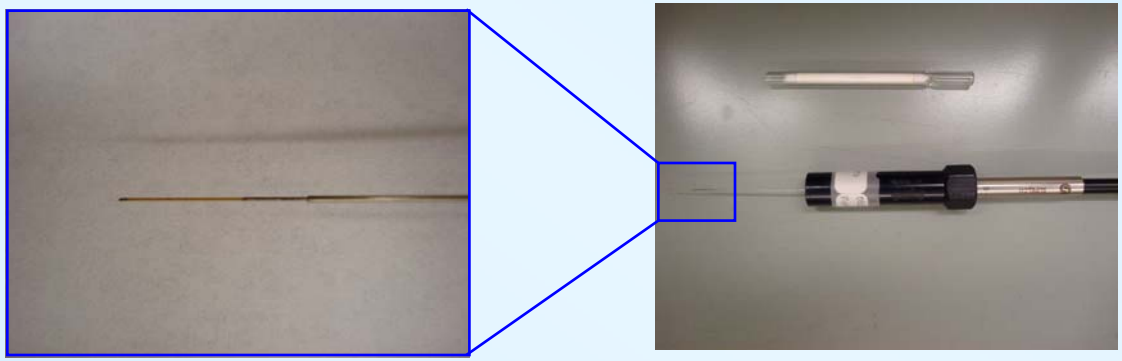
- Quadrupole and ion trap instruments [low mass resolution]
- Electron impact (EI) – [characteristic fragmentations]
- Chemical ionization - positive mode (PCI) [molecular ions]
- Chemical ionization - negative mode (NCI)
  [very sensitive for nitro-PAHs]

Proton NMR

- Identified by 400 MHz ^{1}H NMR: 39 DMNNs/ENNs, two side-chain nitrated DMNs, and 3-methylphthalide.

Sampling of Naphthalene, Alkylnaphthalenes and Phenanthrene

- Sampling onto Tenax cartridges for thermal desorption/GC with flame ionization detection (GC-FID). Used to measure amounts reacted during chamber reactions (calibrate, but gives predictable detector response for organic compounds).



Tenax cartridge

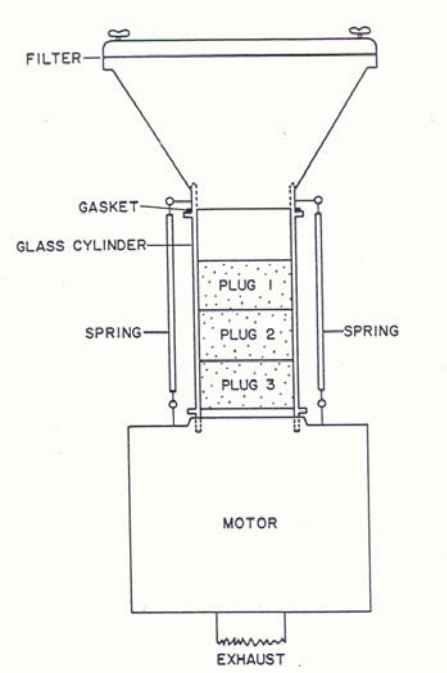
SPME fiber in sampler

Sampling Products for GC/MS Analysis

- Solid Phase Micro-Extraction (SPME) – different fibers for various volatility products and for on-fiber derivatization of carbonyls. Sample chamber contents post-reaction and inject directly into GC/MS. Needs to be calibrated.

Sampling Products for GC/MS Analysis

- Polyurethane foam plugs (PUFs) and filter/PUF combinations – used to sample entire chamber volume for semi-volatile and non-volatile products. Extract with solvent, fractionate by HPLC (if necessary), analyze by GC/MS. (Found some particles "go-through" PUF.)

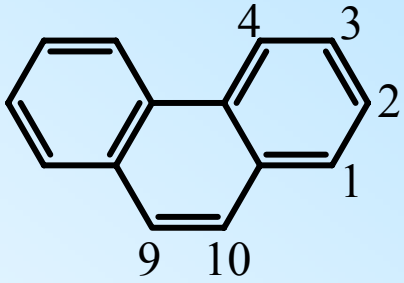


"Operational" gas/particle distribution because:

- gases may be adsorbed onto the filter or onto particles on the filter.
- particle-adsorbed species may "blow-off" the filter (and be collected on the PUFs).

In ambient operation: PUFs collect 3- and 4-ring PAHs and 2-ring nitro-PAHs.

Phenanthrene
(Most abundant 3-ring PAH)



Phenanthrene gas-phase reaction with			
	OH radical[a]	NO_3 radical[b]	Ozone[c]
Lifetimes (τ)	4.3 hr	4.6 hr	41 days

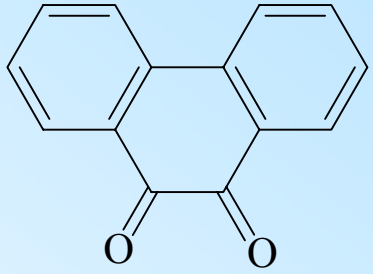
[a] 12-hr daytime average OH radical concentration of 2.0×10^6 molecules cm^{-3}.

[b] 12-hr nighttime average NO_3 radical concentration of 5×10^8 molecules cm^{-3}.

[c] 24-hr average O_3 concentration of 7×10^{11} molecules cm^{-3}.

Note: atmospheric formation of nitro-phenanthrenes expected to be negligible.

9,10-Phenanthrenequinone (9,10-PQ)

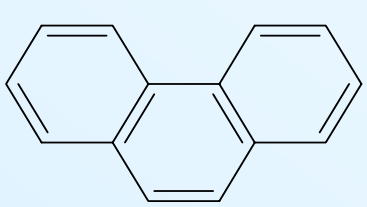


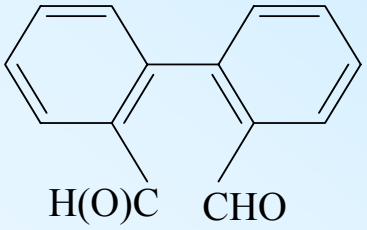
- 9,10-PQ has a favorable reduction potential to undergo redox cycling in biological systems; in aerobic yeast systems, 9,10-PQ exerts toxicity through ROS.[1]
- 9,10-PQ was found in diesel and ambient particles and at elevated concentrations at "downwind sites".[2] 9,10-PQ has been postulated to play a role in the pulmonary toxicity of diesel exhaust particles.[3]
- 9,10-PQ has been observed in ambient air at up to 1 ng m^{-3} and is responsible for the majority of ROS generation in extracts from ambient Fresno, CA particles.[4]

[1]Rodriguez et al., Toxicology, **201**, 185-196 (2004). [2]Cho et al., Aerosol Sci. Technol., **38(S1)**, 68-81 (2004).
[3]Hiyoshi et al., J. Applied Toxicol. **25**, 47-51 (2005). [4]Chung et al., *ES&T.*, **40**, 4880-4886 (2006).

Phenanthrene: abundant, gas-phase, 3-ring PAH in ambient air.

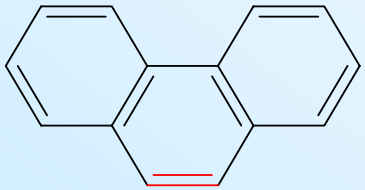
9,10-PQ: relative yields measured with SPME sampling
[Wang et al., Atmos. Environ. **41**, 2025-2035 (2007)].

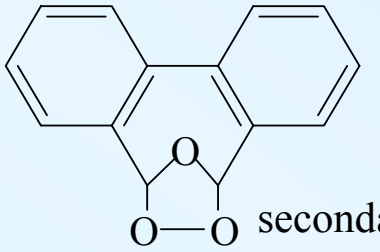




2,2'-diformylbiphenyl

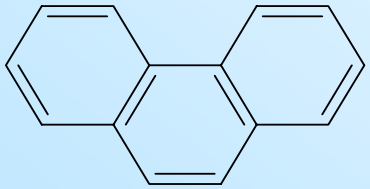
+ 9,10-PQ + other products
[0.10]

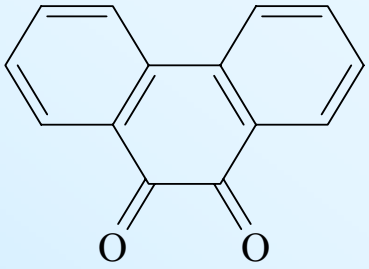




secondary ozonide
from API-MS

+ 9,10-PQ + other products
[0.06]





9,10–phenanthrenequinone

+ other products

PUF/filter samples,
extract, HPLC→
GC/MS.
Calibrate with standard.
33% yield = [1.0]

Ambient Formation of 9,10-Phenanthrenequinone

Assuming: [phenanthrene] = 10 ng m^{-3}

[OH] = 2.0×10^6 radicals cm^{-3}

[NO_3] = 5×10^8 radicals cm^{-3}

[O_3] = 7×10^8 molecules cm^{-3}

$$9,10\text{-PQ} = k_{OH}\,[OH] \times t \times \text{Yield} \times [\text{phen}] = 80 \text{ pg } m^{-3}\, hr^{-1}$$

$$9,10\text{-PQ} = k_{NO3}\,[NO_3] \times t \times \text{Yield} \times [\text{phen}] = 800 \text{ pg } m^{-3}\, hr^{-1}$$

$$9,10\text{-PQ} = k_{O3}\,[O_3] \times t \times \text{Yield} \times [\text{phen}] = 0.2 \text{ pg } m^{-3}\, hr^{-1}$$

Lifetime of phenanthrene in an organic film exposed to 50 ppbv of O_3 was calculated to be 44 days [Kahan et al., Atmos. Environ., **40**, 3448-3459 (2006)].

Recommendations for Future Research

- Ambient measurements should be made of 9,10-phenanthrene quinone to assess the importance of NO_3 radical-initiated formation pathways. Since certain nitro-PAHs, or nitro-PAH ratios, are indicators of NO_3 chemistry, nitro-PAHs should simultaneously be measured.
- Health effects studies designed to specifically address the importance of nighttime NO_3 chemistry should be initiated. An optimum study would have measurements of the NO_3 radical, nitro-PAHs, 9,10-phenanthrene quinone (and other PAH quinones), and an appropriate bioassay and/or biological exposure.

Calculated Tropospheric Lifetimes

PAH	OH[a]	Extreme NO_3[b]	O_3[c]
Naphthalene	5.7 hr	5.3 day	>80 day
1-Methylnaphthalene	3.4 hr	2.7 day	>125 day
2-Methylnaphthalene	2.8 hr	1.9 day	>40 day
Dimethylnaphthalenes	1.8-2.4 hr	1-18 hr	>40 day
Phenanthrene	4.3 hr	28 min	41 day

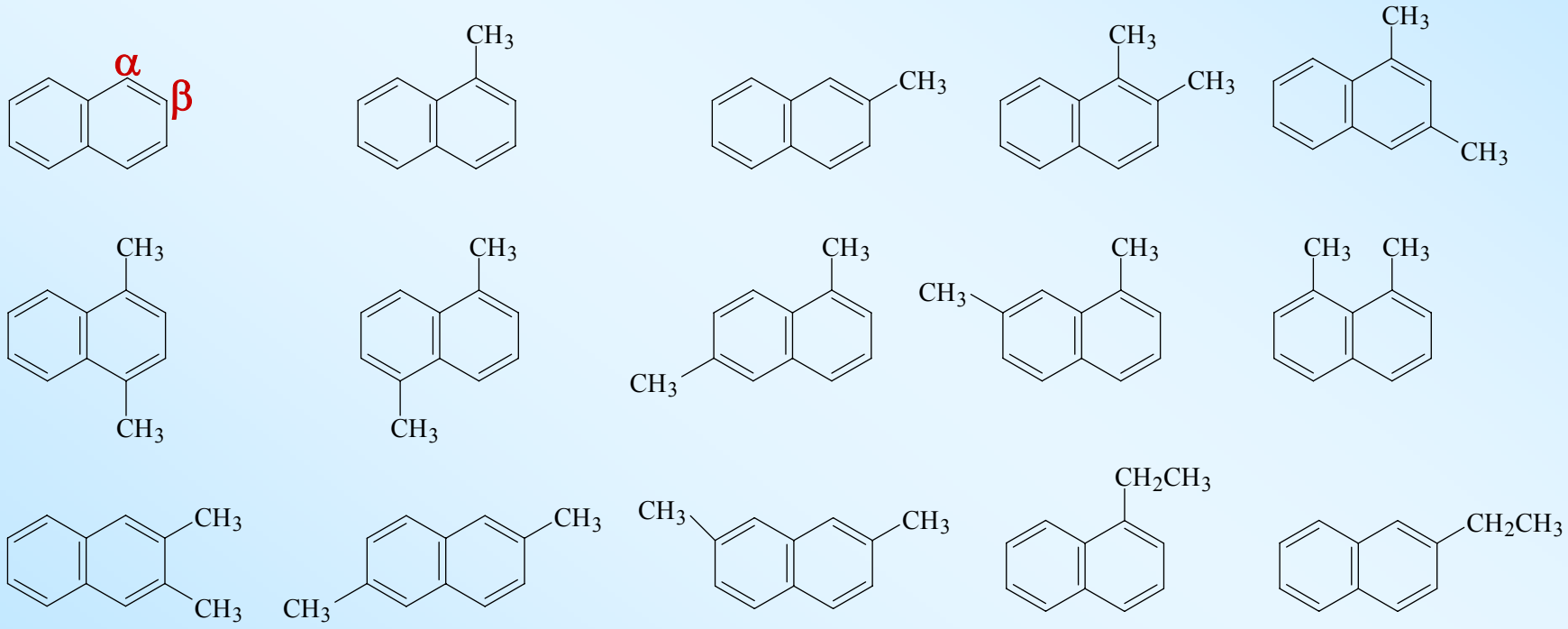
[a]Assumes 12-hr daytime average [OH] = 2×10^6 radicals cm^{-3}.

[b]Assumes 12-hr nighttime average [NO_3] = 5×10^9 radicals cm^{-3} (100 ppbv NO_2).

[c]Assumes 24-hr average [O_3] = 7×10^{11} molecules cm^{-3} (30 ppbv).

Chamber hydroxyl (OH) radical-initiated reactions of:

Naphthalene, 1- and 2-MN, 10 DMNs, 1- and 2-EN



In a series of chamber reactions, API-MS analyses of OH + naphthalene, 1- and 2-methylnaphthalene (MN), the 10 dimethylnaphthalenes (DMNs) and the ethylnaphthalenes (ENs) showed quinone products were minor.

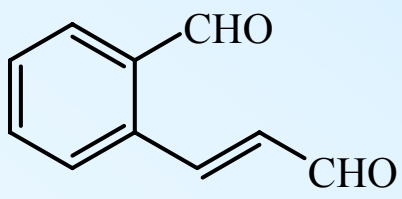
API-MS analyses showed major products were:

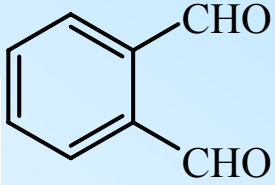
1. Ring-opened dicarbonyls (32 mass units above parent MW).
2. Ring-opened dicarbonyls of lower MW resulting from loss of two β-carbons (and associated alkyl groups).

   Shown to be at least partly primary in naphthalene system.
3. Ring-containing products that may be epoxides.

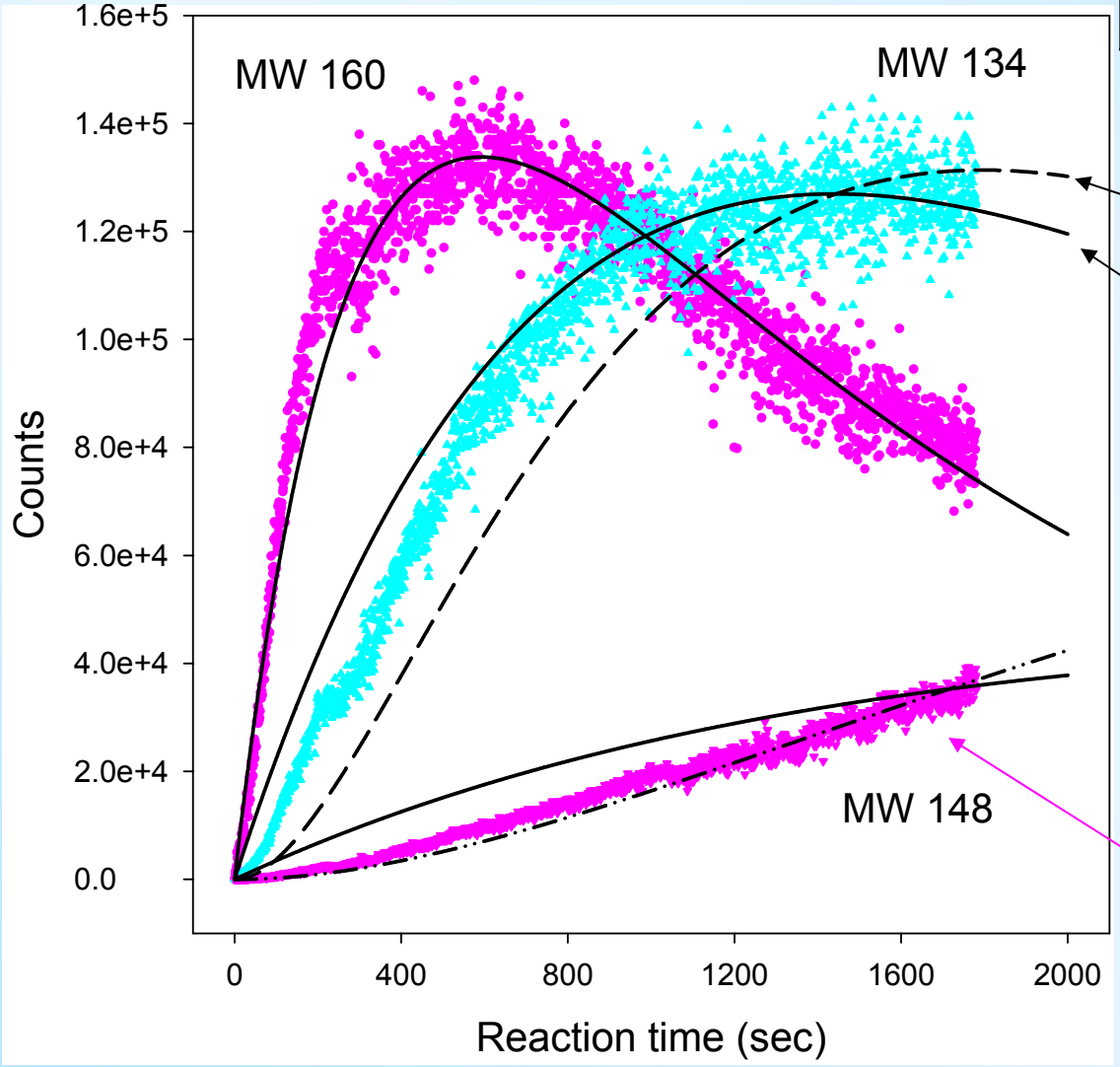
SPME GC/MS analyses (in addition to above, showed):

4. Anhydride secondary products. [Potential source of phthalic acids suggested as markers of secondary organic aerosol (SOA).] Shown to be 2ndary in naphthalene system.



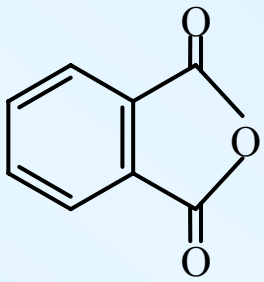


Atmospheric chemistry studied



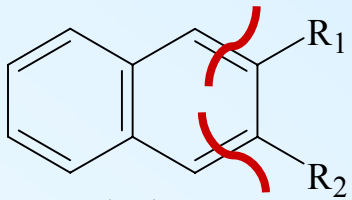
dashed line 2nd generation

solid line 1st generation



Atmospheric chemistry studied

2nd generation from 1st generation phthaldialdehyde



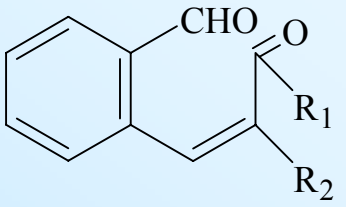
+ OH

naphthalene: $R_1,R_2 = H$

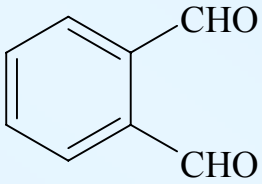
2-MN: $R_1 = CH_3$; $R_2 = H$

2-EN: $R_1 = CH_3CH_2$; $R_2 = H$

2,3-DMN: $R_1,R_2 = CH_3$



#1 parent MW + 32

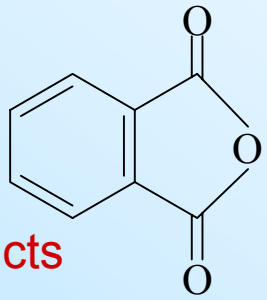


phthaldialdehyde

#2 loss of 2 β-carbons

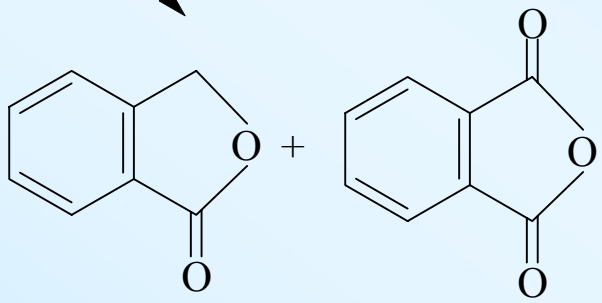
OH

hν



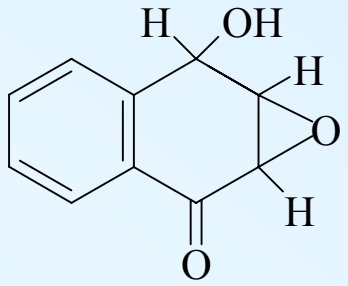
#4 2ndary products

phthalic anhydride



phthalide

#3 epoxides

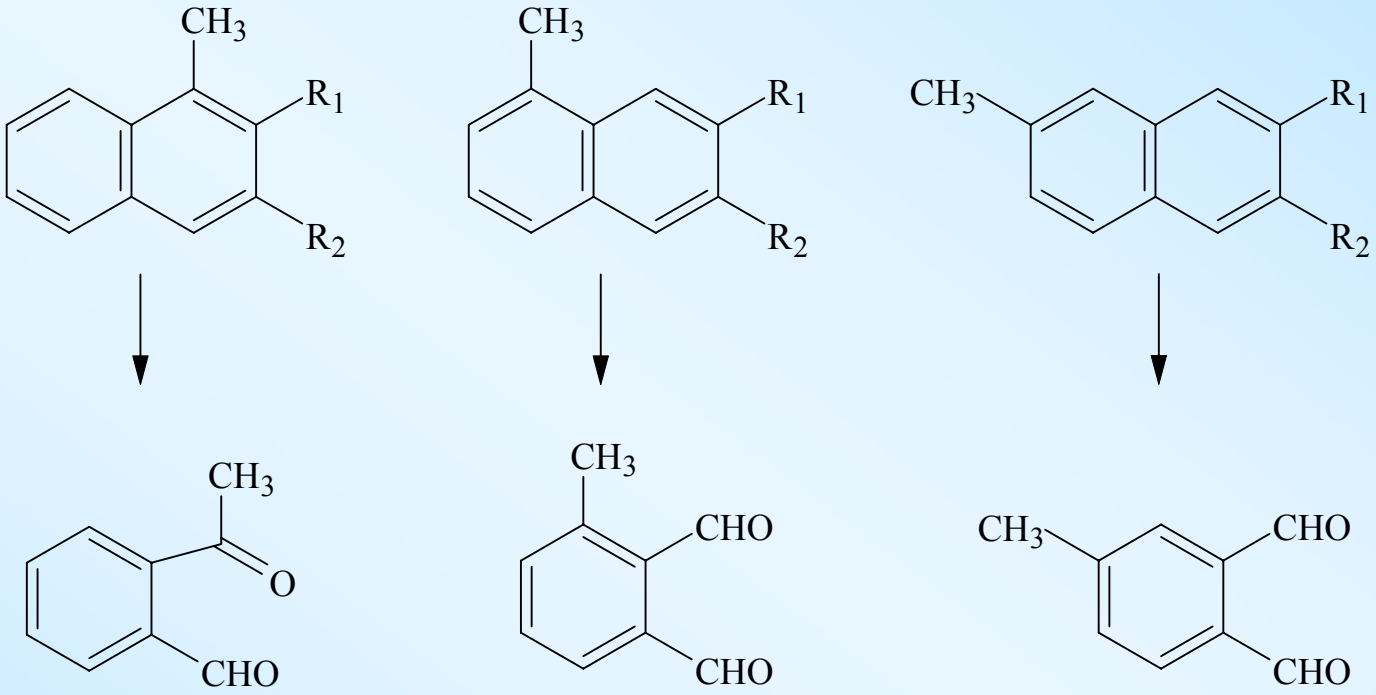


from naphthalene

Phthalic acid suggested marker for SOA.

Consistent products from naphthalene-d_8, 1-MN-d_{10} and 2-MN-d_{10}

MW 148 species, resulting from the loss of two β-carbons from the MNs and two β-carbons and an associated alkyl group from the DMNs.



2-Acetylbenzaldehyde

1-MN: $R_1,R_2 = H$ [86%]
1,2-DMN: $R_1 = CH_3$; $R_2 = H$
1,3-DMN: $R_1 = H$; $R_2 = CH_3$

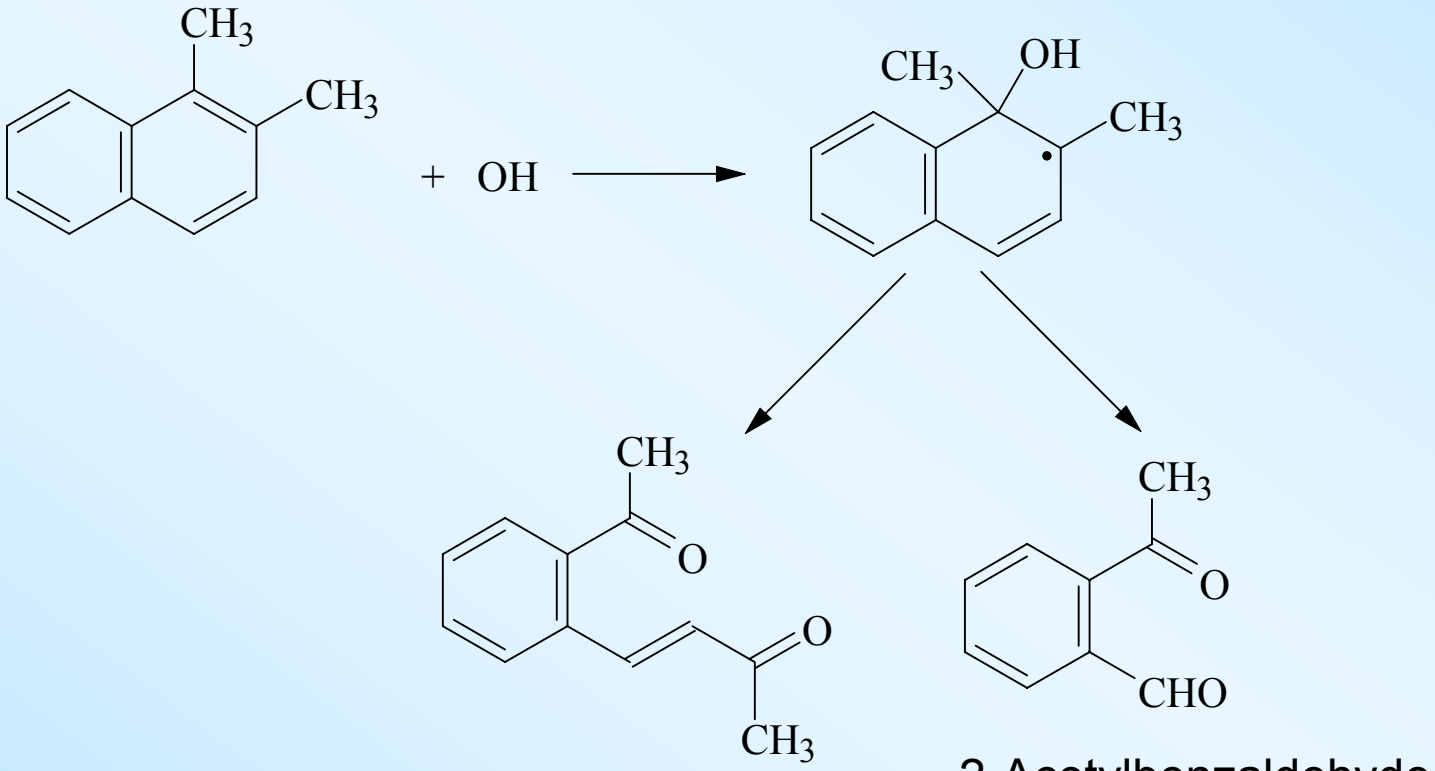
1-MN: $R_1,R_2 = H$ [14%]
1,6-DMN: $R_1 = H$; $R_2 = CH_3$
1,7-DMN: $R_1 = CH_3$; $R_2 = H$

2-MN: $R_1,R_2 = H$
2,6-DMN: $R_1 = H$; $R_2 = CH_3$
2,7-DMN: $R_1 = CH_3$; $R_2 = H$

2-Acetylbenzaldehyde confirmed with standard

Relative amounts of MW 148 products based on GC/MS CI peak areas. OH preferentially attacks the substituted ring.

Dicarbonyl products are generally consistent with the OH radical adding preferentially to the position *ortho* to alkyl-substitution. However, products of 1,2-DMN are consistent with ring-opening between C_1 and C_2, implying *ipso* addition of OH to ring.



2-Acetylbenzaldehyde

Sole MW 188 product.

Identification based on MS fragmentation.

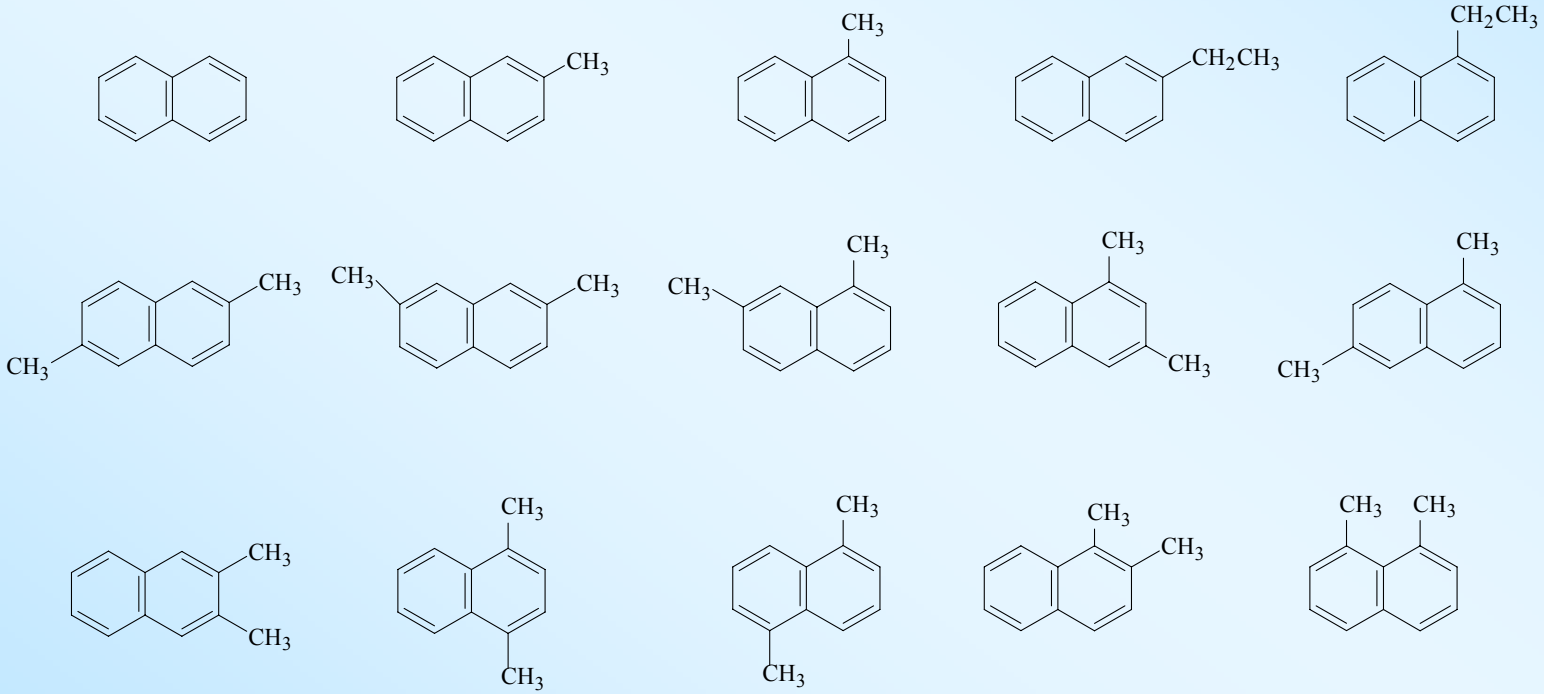
Recommendations for Future Research

- We have identified a suite of oxygenated products from the OH radical-initiated reactions of the alkylnaphthalenes and the presence of these products in ambient air should be examined, as well as their potential toxicity. These products include reactive unsaturated dicarbonyls and epoxides. Additionally, glyoxal, methylglyoxal and biacetyl are the expected co-products when the alkylnaphthalene-OH adducts decompose by loss of adjacent β-carbons.

Chamber nitrate (NO_3) radical-initiated reactions of:

Naphthalene, 1- and 2-MN, ten DMNs, 1- and 2-EN.

Assess formation of quinones and of nitro-products, some of which may photolyze to form quinones.



Isomers shown in their elution order on a 5% phenylmethyl-siloxane capillary column.

Genotoxicity and Carcinogenicity of Nitro-PAHs

+ bacterial assays
+ human cell assays
+ animal carcinogen

Identified in Diesel Exhaust Particles

+ + +	1-nitropyrene
+ + +	2-nitrofluorene
+ + +	1,6- and 1,8-dinitropyrene
+ + +	6-nitrochrysene
+ +	3-nitrobenzanthrone

Identified as Products of Atmospheric Reactions of PAHs

+ +	2-nitrofluoranthene
+ + +	2-nitropyrene
+ +	nitronaphthalenes
+	methylnitronaphthalenes
+ +	2-nitrodibenzopyranone
+ +	nitropyrene lactones

"Nitro-PAHs are probably human carcinogens"*

*IPCS Environmental Health Criteria 229, WHO, Geneva (2003).

Gas-phase PAHs

Particle-associated PAHs

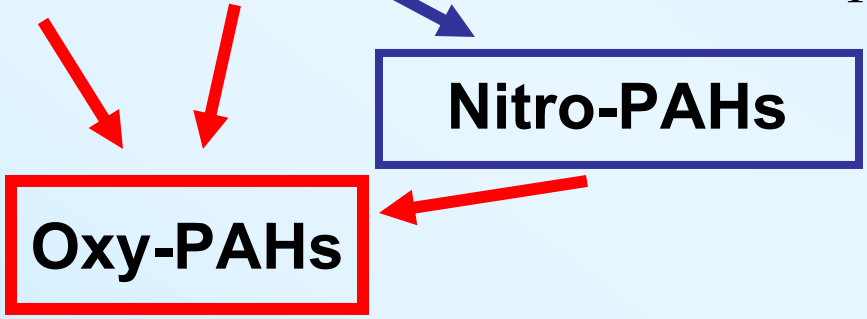
OH Radical - Daytime

NO_3 Radical - Nighttime

Photolysis (also OH Radical?)

Ozone – 24 hrs.

NO_2/HNO_3 – 2ndary



Particle-associated

Fluoranthene **(g)** + OH ⟶ 2-Nitrofluoranthene (3% yield)

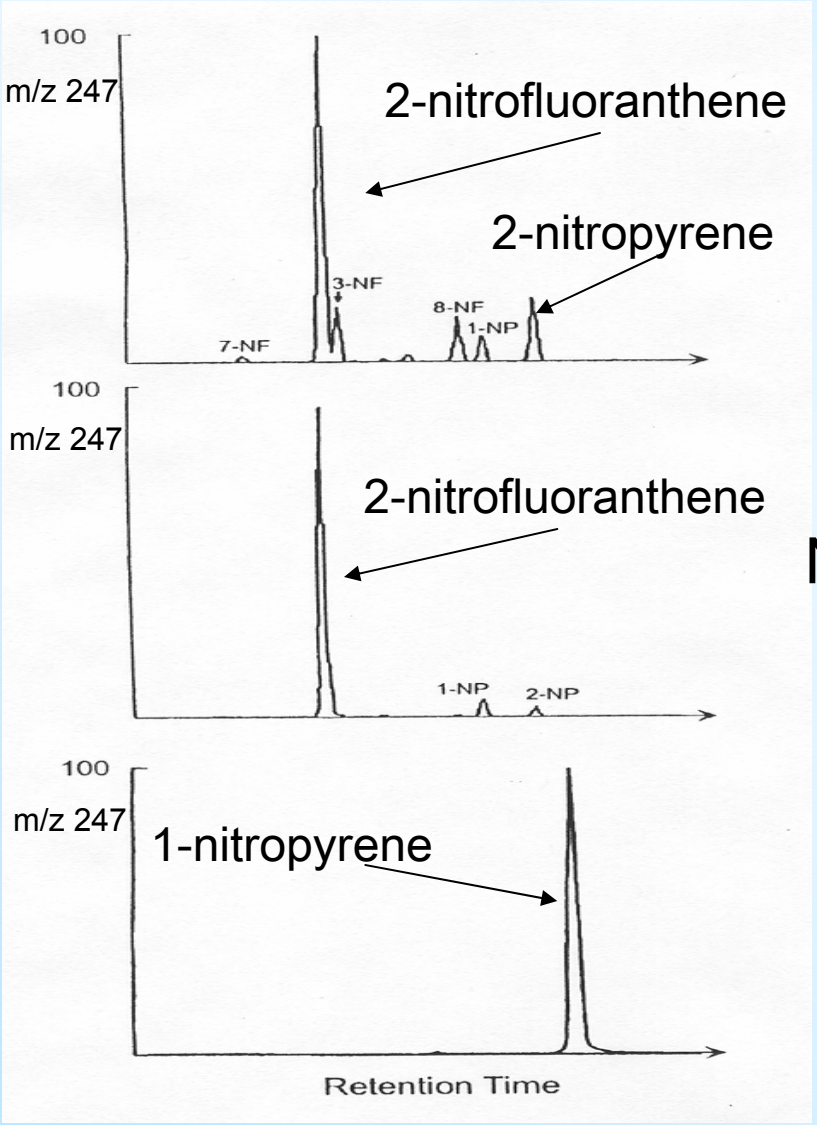
Fluoranthene **(g)** + NO_3 ⟶ 2-Nitrofluoranthene (24% yield)

Fluoranthene **(s)** + HNO_3/NO_2 ⟶ 3-Nitrofluoranthene

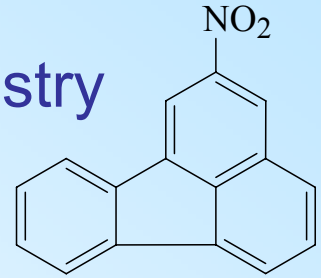
Pyrene **(g)** + OH ⟶ 2-Nitropyrene (0.5% yield)

Pyrene **(s)** + HNO_3/NO_2 ⟶ 1-Nitropyrene

Nitro-PAHs in ambient particles are dominated by isomers formed in the atmosphere from gas-phase reactions.



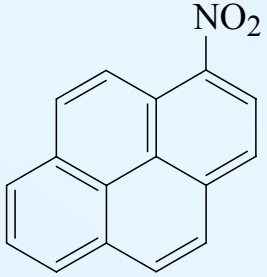
OH Radical Chemistry
Daytime
Torrance, CA



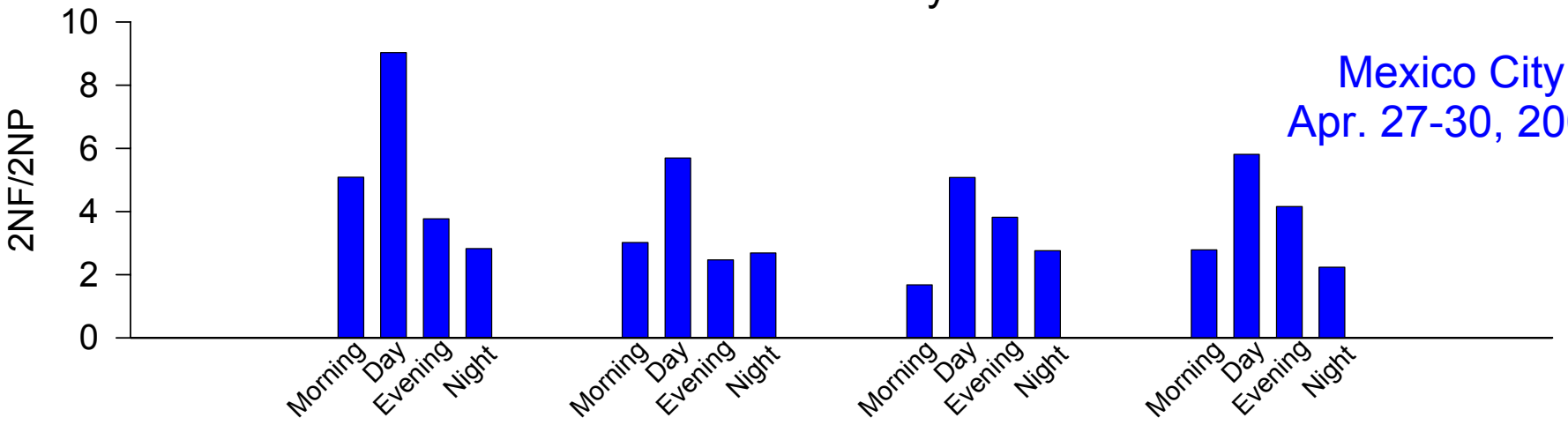
Gas-phase radical-initiated reactions leading to less volatile particle-associated products.

NO_3 Radical Chemistry
Nighttime
Claremont, CA

Diesel Particles

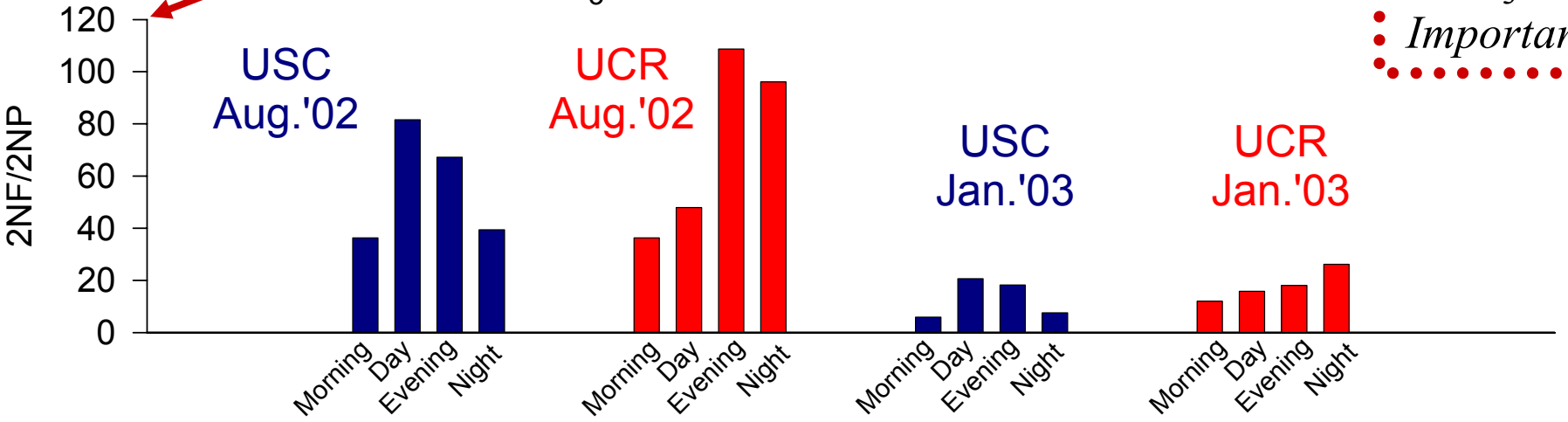


The ratio 2-nitrofluoranthene/2-nitropyrene (2NF/2NP) < 10
indicates OH chemistry dominates.

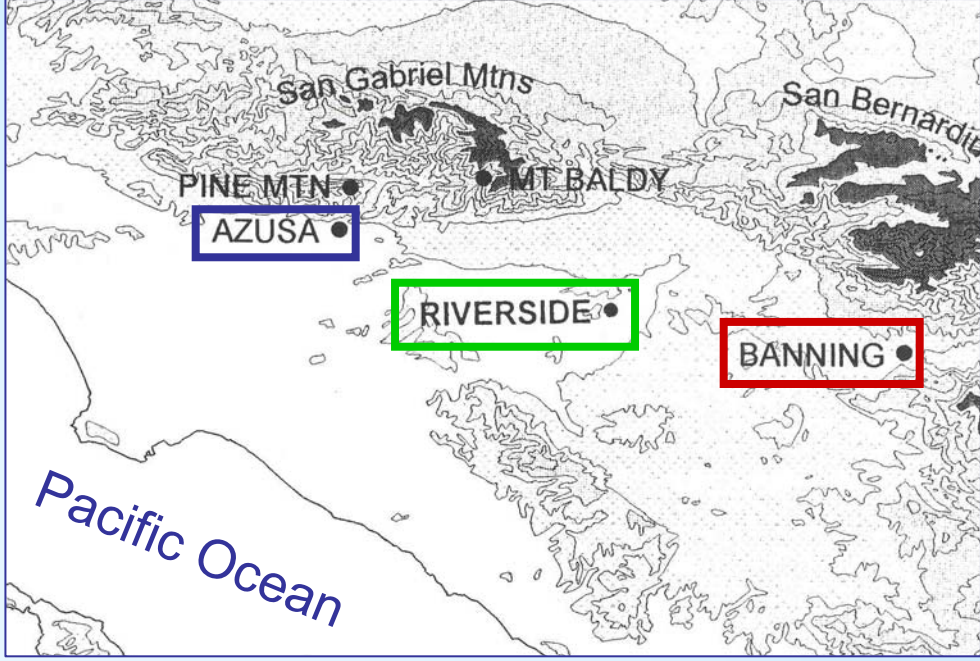


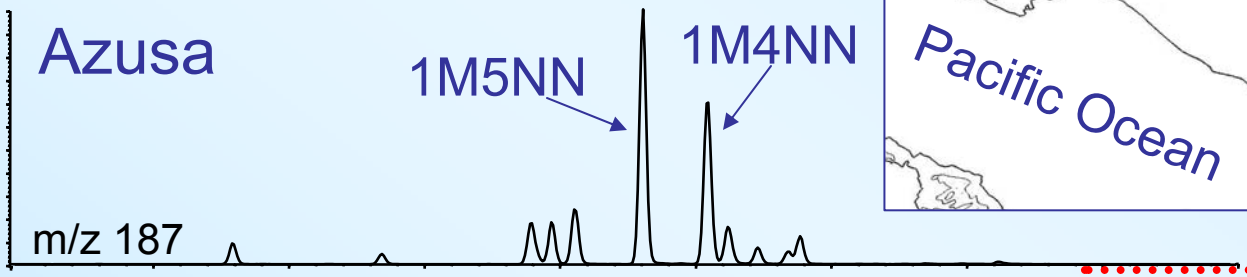
The ratio 2NF/2NP large,
suggests NO_3 radical formation of 2-nitrofluoranthene.

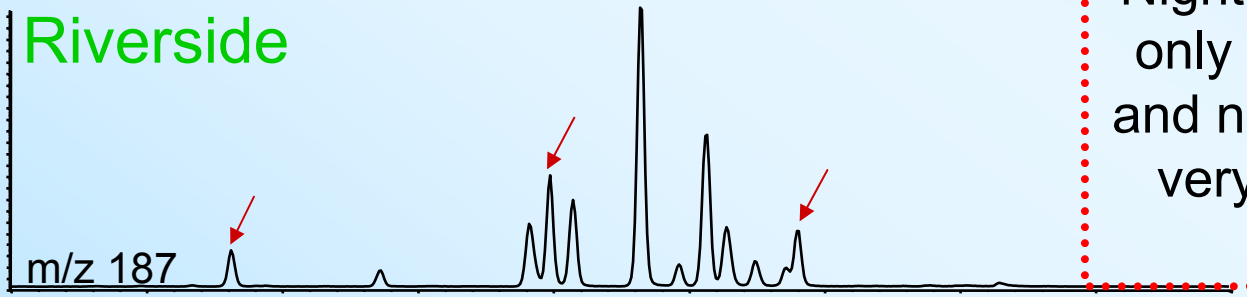
In So.Cal. NO_3 is Important.

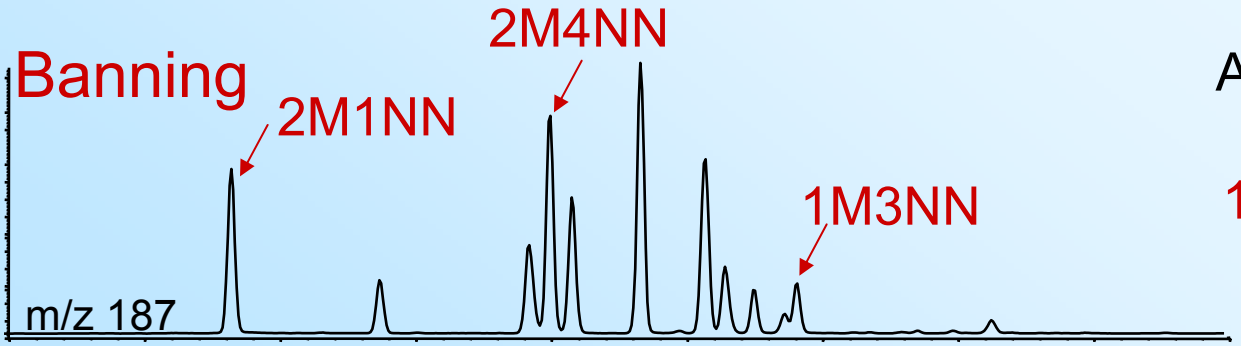


Methylnitronaphthalenes (MNNs) result from OH or NO_3 radical reactions of 1- and 2-methylnaphthalene. At Azusa OH chemistry dominates (markers: 1M5NN, 1M4NN). Downwind markers of NO_3 radical reactions increase.









Nighttime samples shown. If only OH chemistry, daytime and nighttime samples will be very similar – as at Azusa and Mexico City.

At Banning increased 2M1NN, 2M4NN & 1M3NN indicate NO_3 reactions.

Task 4: Conduct synthesis of dimethylnitronaphthalenes.

- Reactions of dimethylnaphthalenes with N_2O_5 in CCl_4 solution expected to give isomers similar to those formed by NO_3 in the gas phase.

- Synthesis will allow identification of dimethylnitro-naphthalenes formed in OH and NO_3 radical reactions of 1,6-DMN, 1,7-DMN, 2,6-DMN and 2,7-DMN.

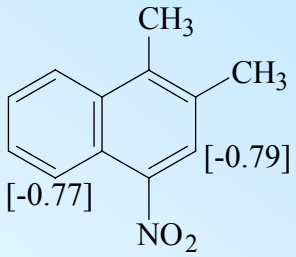
- Synthesis will produce sufficient dimethylnitro-naphthalenes for photolysis studies.

Conducted nitrations with N_2O_5 in CCl_4 for all ten DMNs and both ENs. We were able to report the EI mass spectra and retention indices (on a 5% phenylmethyl-siloxane capillary column) of all 42 DMNNs (with NMR characterization of 32 of these) and of 11 of the 14 ENNs (with NMR characterization of 7 of these). Three assignments were tentative.

For each DMN there are either 3 or 6 DMNN isomers and for each EN there are 7 ENN isomers.

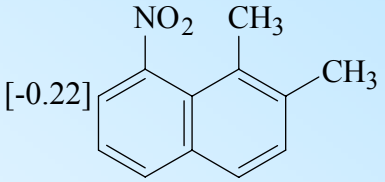
The 42 DMNNs isomers can be divided into 6 groups with characteristic EI mass spectral fragmentation, GC retention behavior and characteristic chemical shifts of the protons influenced by the NO_2 group.

1. DMNN isomers with NO_2 substitution on an α-carbon and no steric interaction with the methyl substituents.

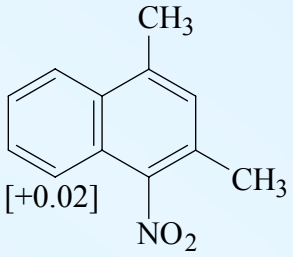


Shift of protons *ortho* or *peri* to NO_2 is 0.6-0.9 ppm

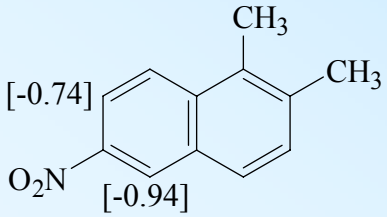
2. DMNN isomers with NO_2 and CH_3 substituents in *peri* positions.



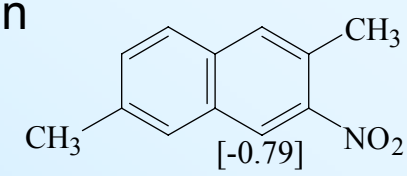
3. DMNN isomers with NO_2 substitution on an α-carbon and with an *ortho* CH_3 group.



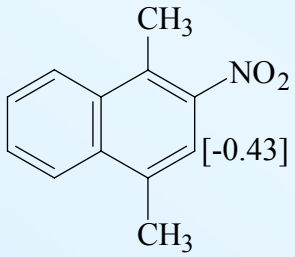
4. DMNN isomers with NO_2 substitution on a β-carbon and no steric interaction with the methyl substituents.



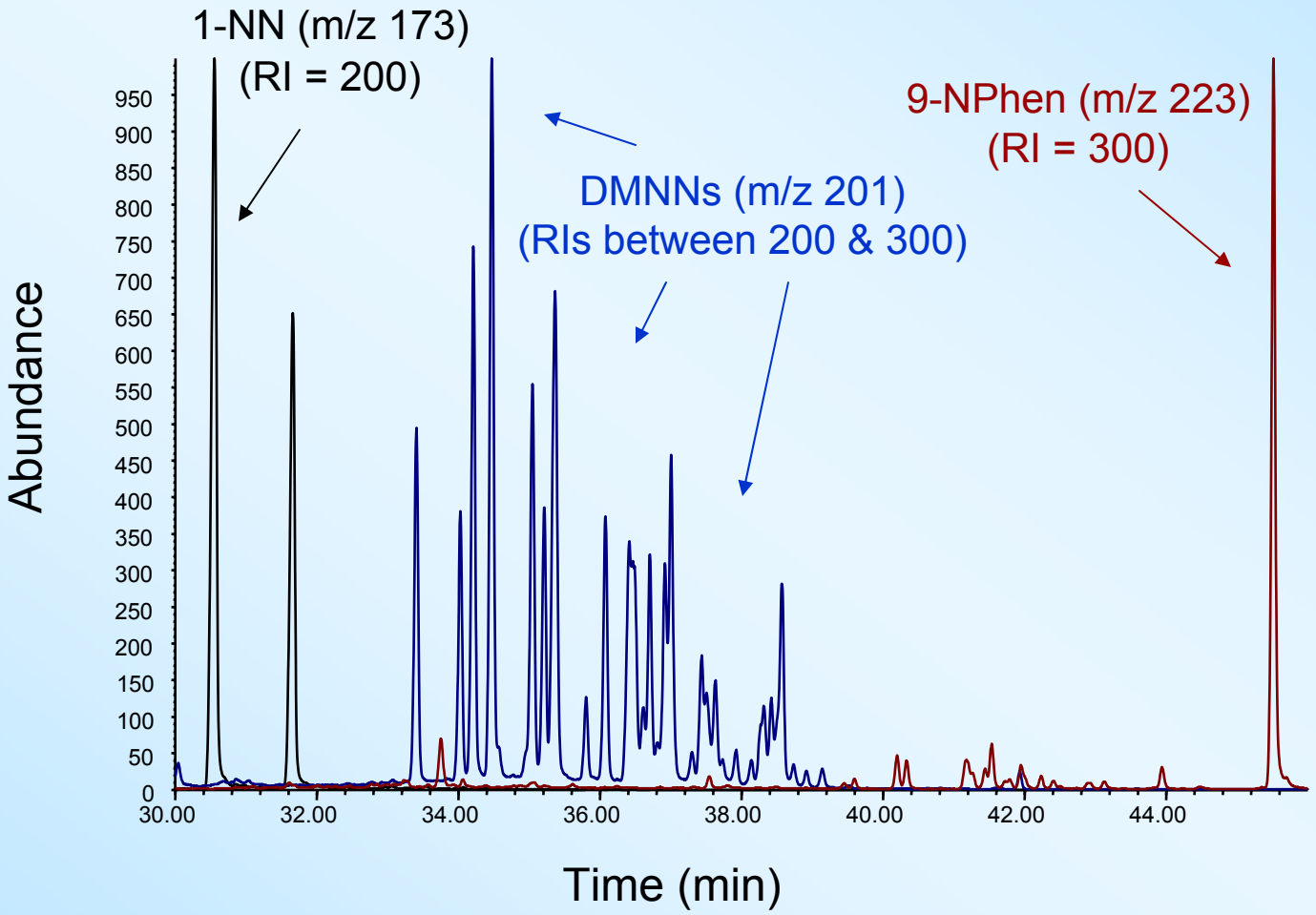
5. DMNN isomers with NO_2 substitution on a β-carbon and an *ortho* CH_3 group also on a β-carbon

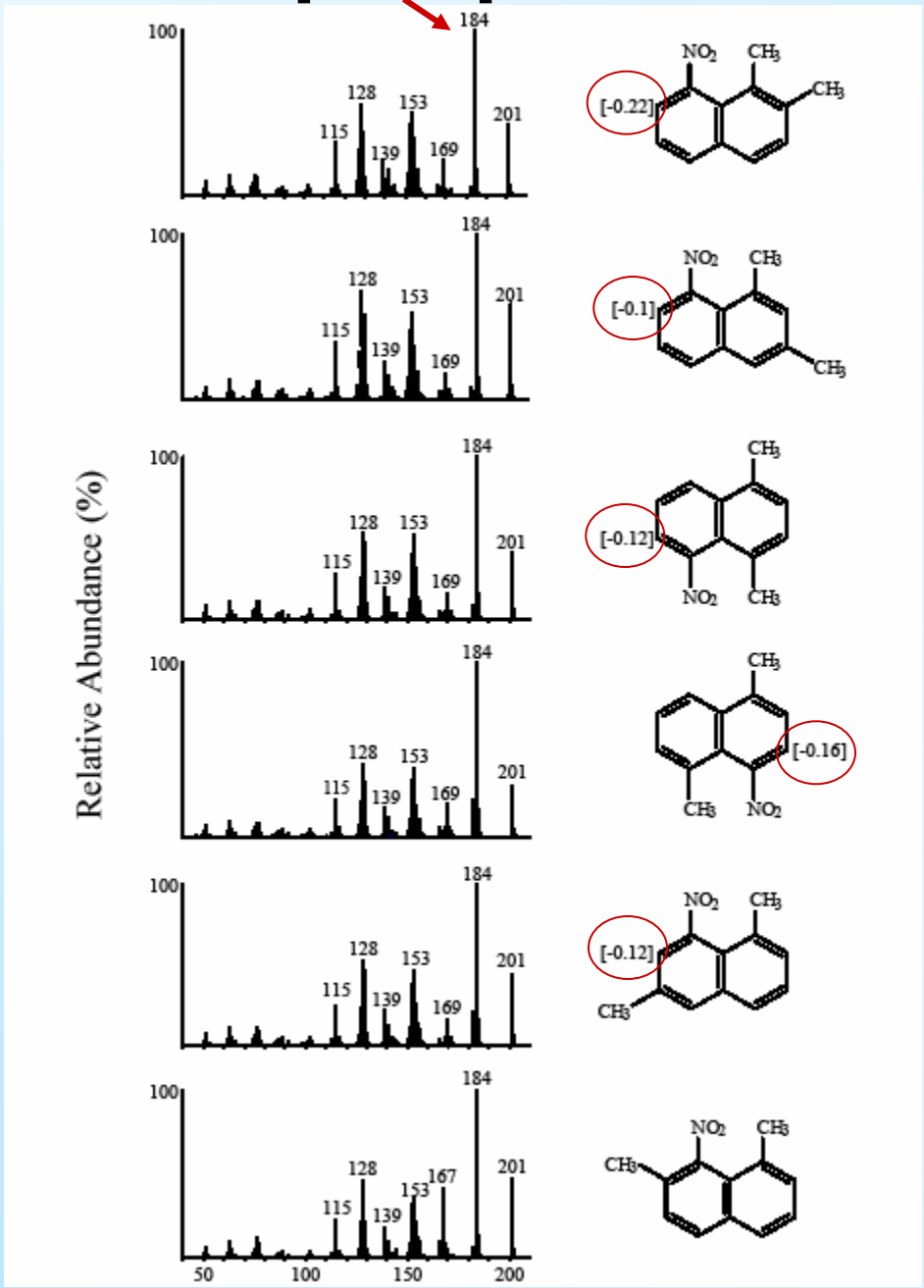


6. DMNN isomers with NO_2 substitution on a β-carbon and an *ortho* CH_3 group on an α-carbon.



Retention Indices (RI)



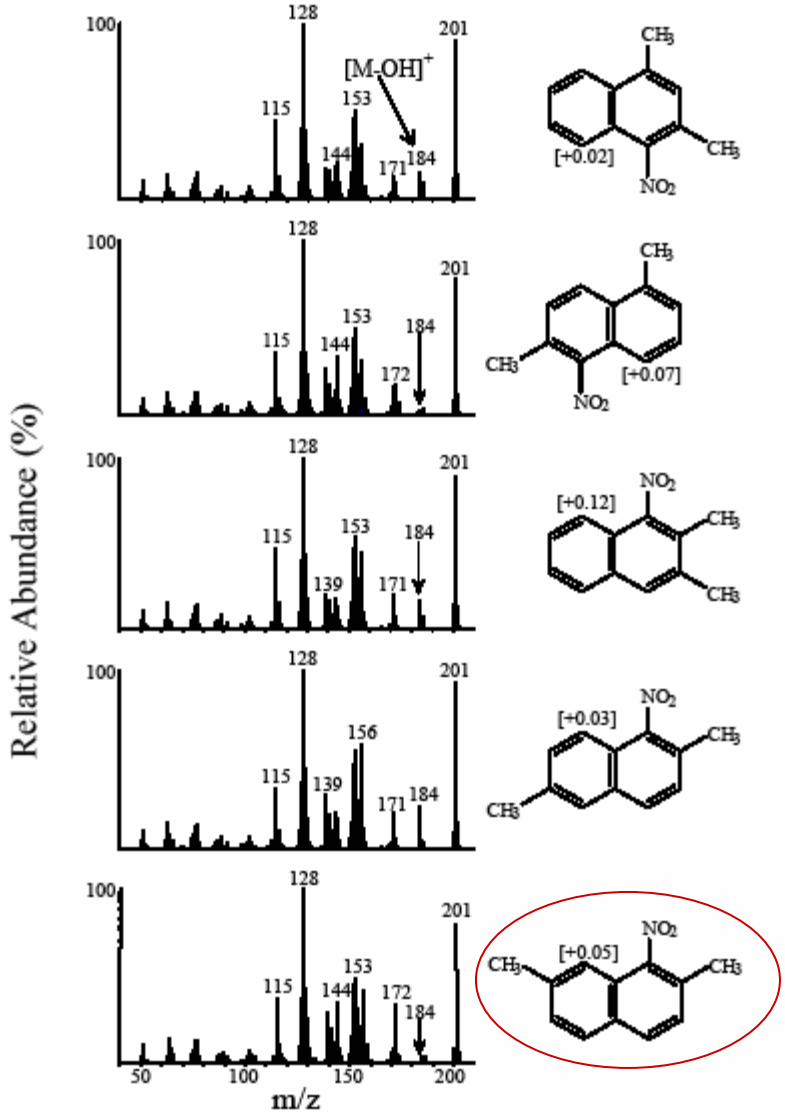


2. DMNN isomers with NO_2 and CH_3 substituents in *peri* positions.

Characteristic fragmentation: $[M\text{-}OH]^+$ is the base peak in the EI spectra.

The NO_2 group is anisotropic (electron density around C-NO_2 bond is not symmetric). Crowding of *peri* CH_3 and NO_2 groups twists the NO_2 and causes the proton *ortho* to NO_2 to have only a very slight downfield shift from its position in the parent DMN.

These peri-substituted isomers elute early. For example, 1,2-DM-8NN elutes 1st of the six 1,2-DMNN isomers.

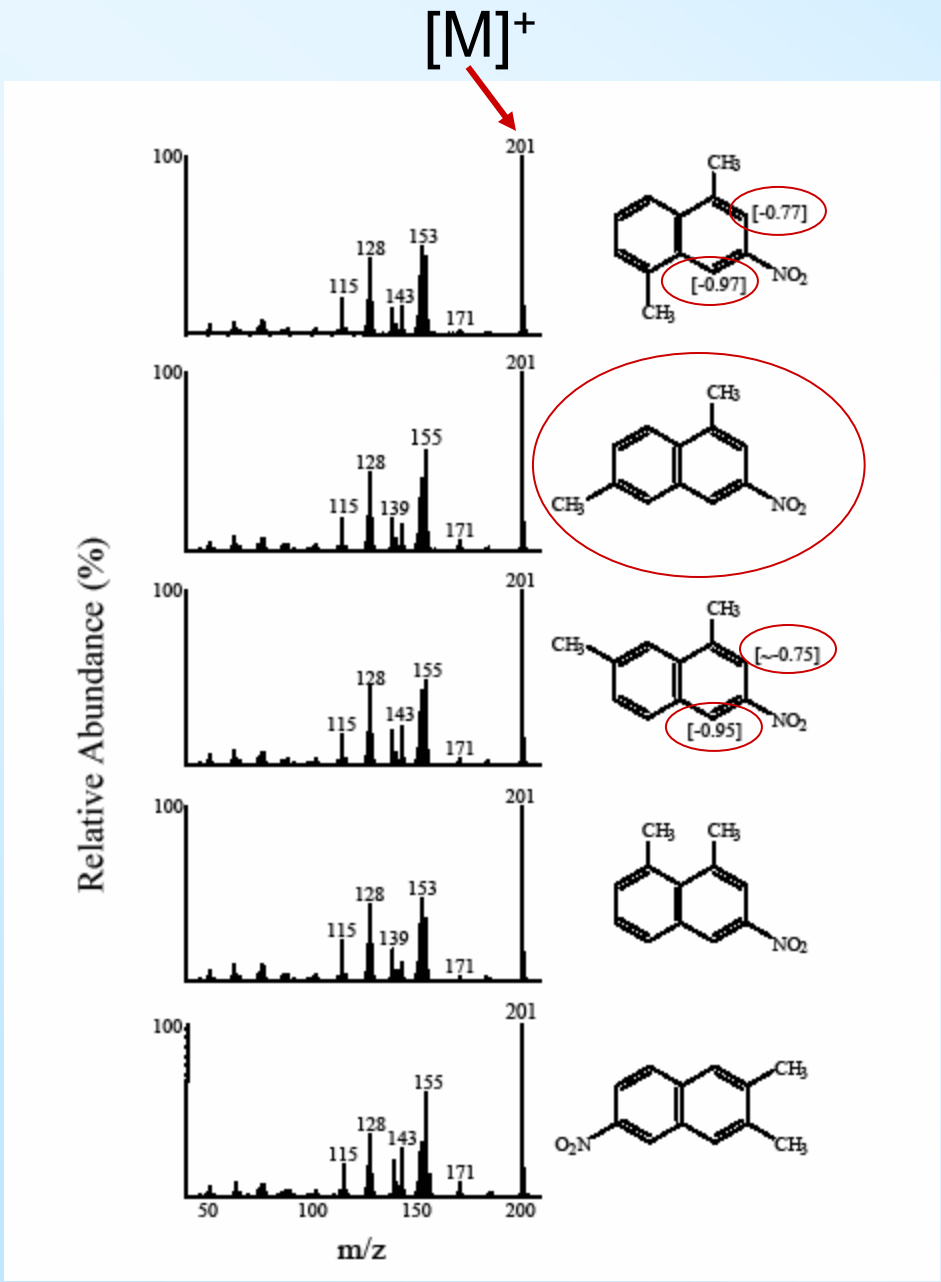


3. DMNN isomers with NO_2 substitution on an α-carbon and with an *ortho* CH_3 group.

Characteristic fragmentation: $[M\text{-}OH]^+$ at m/z = 184 is present in the EI spectra.

The chemical shift of the proton *peri* to the NO_2 is **upfield** from its position in the parent DMN.

Interaction (hydrogen bonding) of the CH_3 and NO_2 group reduces the polarity of the molecule and these elute early. For example, 2,7-DM-1NN elutes 1st of the three 2,7-DMNN isomers.



4. DMNN isomers with NO_2 substitution on a β-carbon and no steric interaction with the methyl substituents.

Note that the molecular ion, $[M]^+$ at m/z =201 is the base peak in all these spectra.

The "uncrowded" NO_2 group is in the plane of the naphthalene ring and causes large downfield shifts for the protons *ortho* to the NO_2 group.

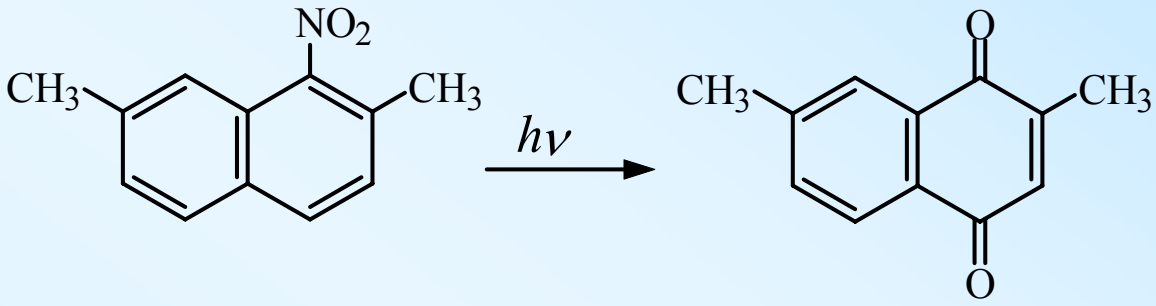
Consistent with 2-NN eluting after 1-NN, each of these isomers elutes last of the isomers from a given DMN parent. For example, 1,6-DM-3NN elutes last of the six 1,6-DMNN isomers.

Amounts of Dimethylnitronaphthalene crystals produced (purities).

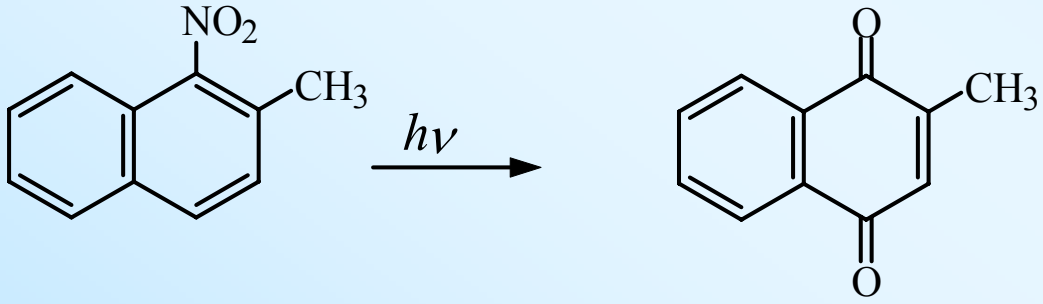
> 200 mg	40-100 mg	10-20 mg
2,6-DM-1NN (>99%)	1,2-DM-4NN (>98%)	1,6-DM-4NN (>99%)
	1,3-DM-4NN (>99%)	1,7-DM-4NN (>98%)
	1,5-DM-4NN (>99%)	1,8-DM-2NN (~87%)
	1,6-DM-5NN (>99%)	2,3-DM-5NN (>99%)
	1,7-DM-8NN (>99%)	2,6-DM-4NN (>98%)
	1,8-DM-4NN (>99%)	2,7-DM-1NN (>99%)
	2,3-DM-1NN (>99%)	

- Retention indices and mass spectra sufficient to identify the DMNNs/ENNs produced in NO_3 and OH radical-initiated reactions. For ambient analyses, many “co-elutions” are a problem.

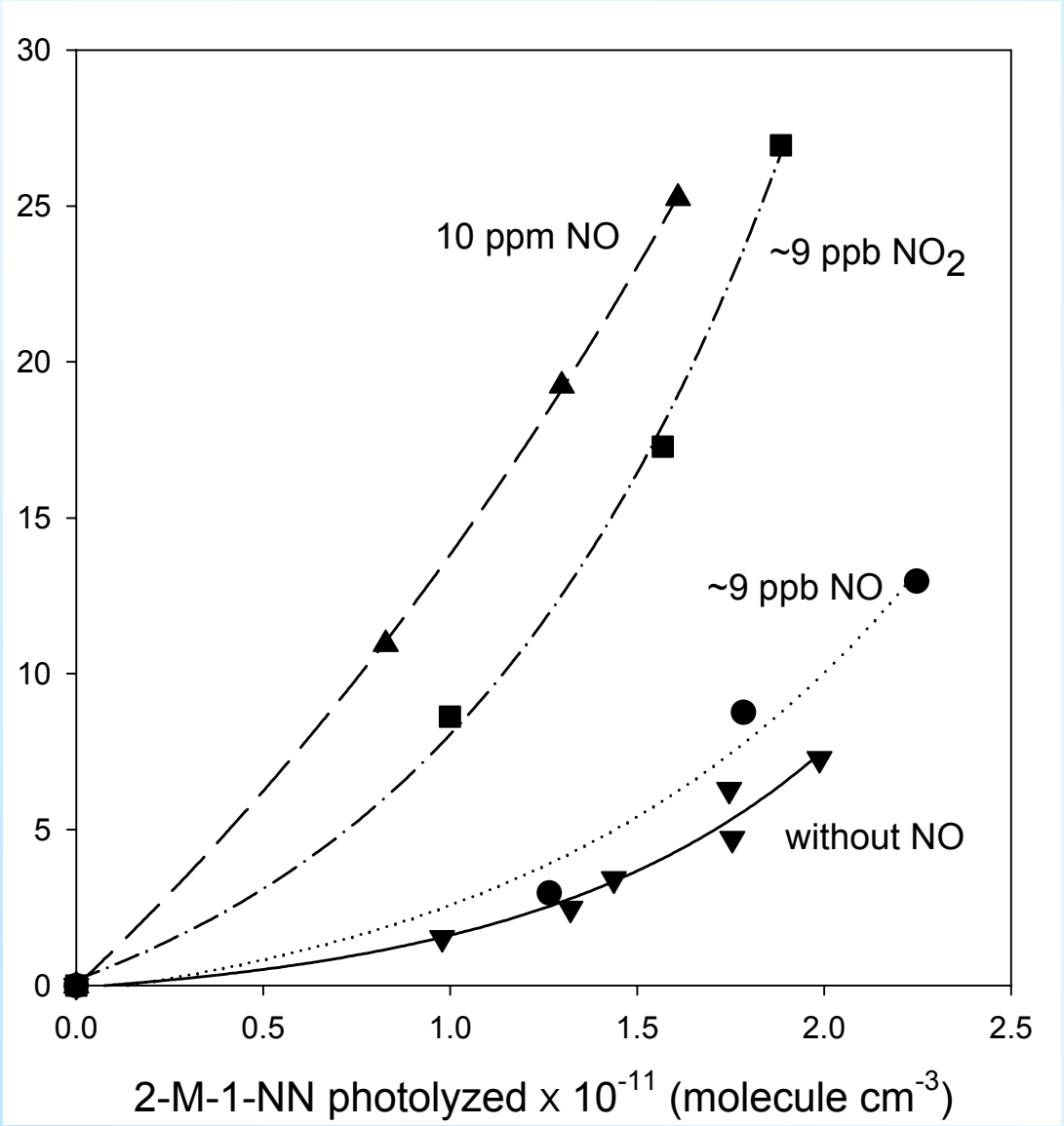
Photolysis of 2,6-DM-1NN gave 2,6-DM-1,4-naphthoquinone.



Photolysis of 2-M-1NN gave 2-M-1,4-naphthoquinone as previously reported, but a very low yield was measured in the absence of NO_x.



Formation of 2-methyl-1,4-naphthoquinone (2-M-1,4-NQ) from photolysis of 2-M-1NN under varied starting NO_x concentrations. The lines are for illustrative purposes only.



NO_x dependence surprising, possibly a chamber artifact???

MTC gave lower yields of DMNN from DMN + NO_3 at low NO_x than the ITC. Also, heterogeneous product formation (side-chain nitro discussed below) very high in MTC.

Recommend additional experiments.

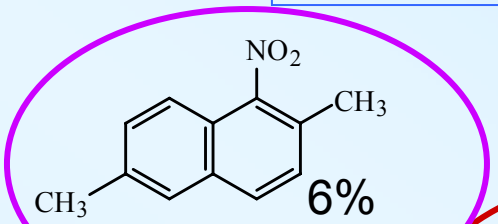
Task 3: Identification of dimethylnitronaphthalenes from the OH and NO_3 radical-initiated reactions of 1,6-, 1,7-, 2,6- and 2,7-dimethylnaphthalenes (the most abundant isomers observed in ambient air samples).

- OH Radical-initiated reactions of 1,6-, 1,7-, 2,6- and 2,7-DMN gave low yields of DMNNs. Yields not quantified, but DMNN/ENN profile produced from reaction of ambient surrogate DMN/EN mixture. Profile of DMNNs/ENNs from NO_3 radical-initiated reaction of ambient DMN/EN mixture also produced.
- DMNN and ENN profiles determined and yields measured individually for all 10 DMNs and 1- and 2-EN reacting with the NO_3 radical (yields determined by GC-FID). The yields of quinones formed were also determined. Examining the effect of the NO_2 concentration is an on-going investigation.

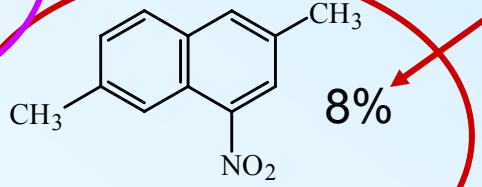
NO_3 Radical-Initiated Reaction of DMNs/ENs (Σ300 ppbv)

2-EN	1,6-DMN			1,2-DMN
2,6-DMN	1,7-DMN			2,3-DMN
2,7-DMN	1,3-DMN	1-EN	1,4-DMN	1,5-DMN
1:	0.7:	0.5:	0.3:	0.2

GC/MS-NCI
m/z 201



2,6-DM-1NN*



2,6-DM-4NN*

2,7-DM-1NN

2E-1NN

1,7-DM-8NN

1,6-DM-5NN

2E-4NN*

2E-8NN

2,7-DM-4NN*

1,2-DM-4NN*

32

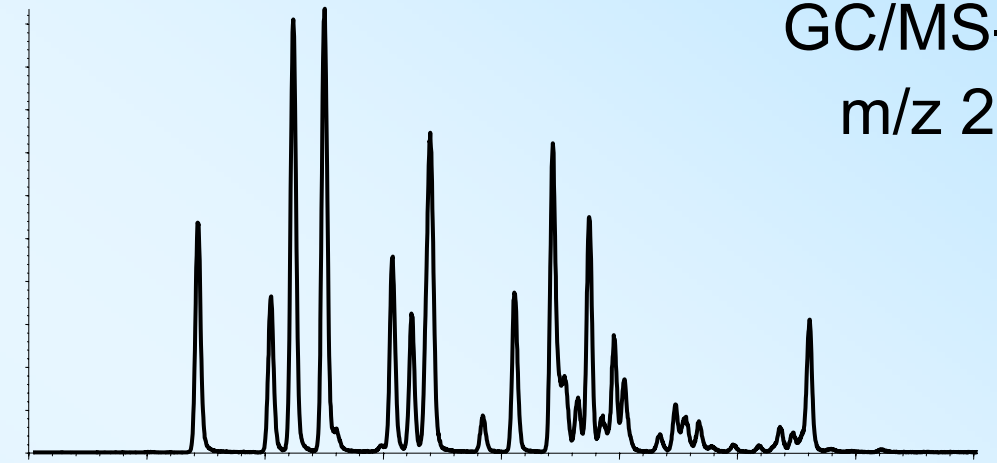
Retention Time →

40 min

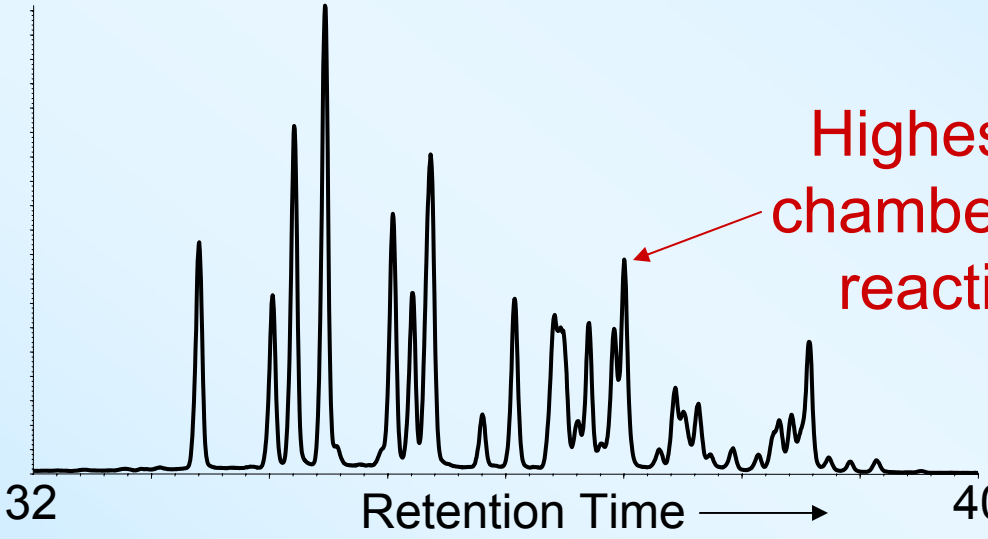
*additional isomer(s)

DMNNs/ENNs from chamber reaction of NO_3 with DMNs/ENs

GC/MS-NCI
m/z 201



DMNNs/ENNs in HPLC fraction of nighttime PUF sample from Redlands, CA

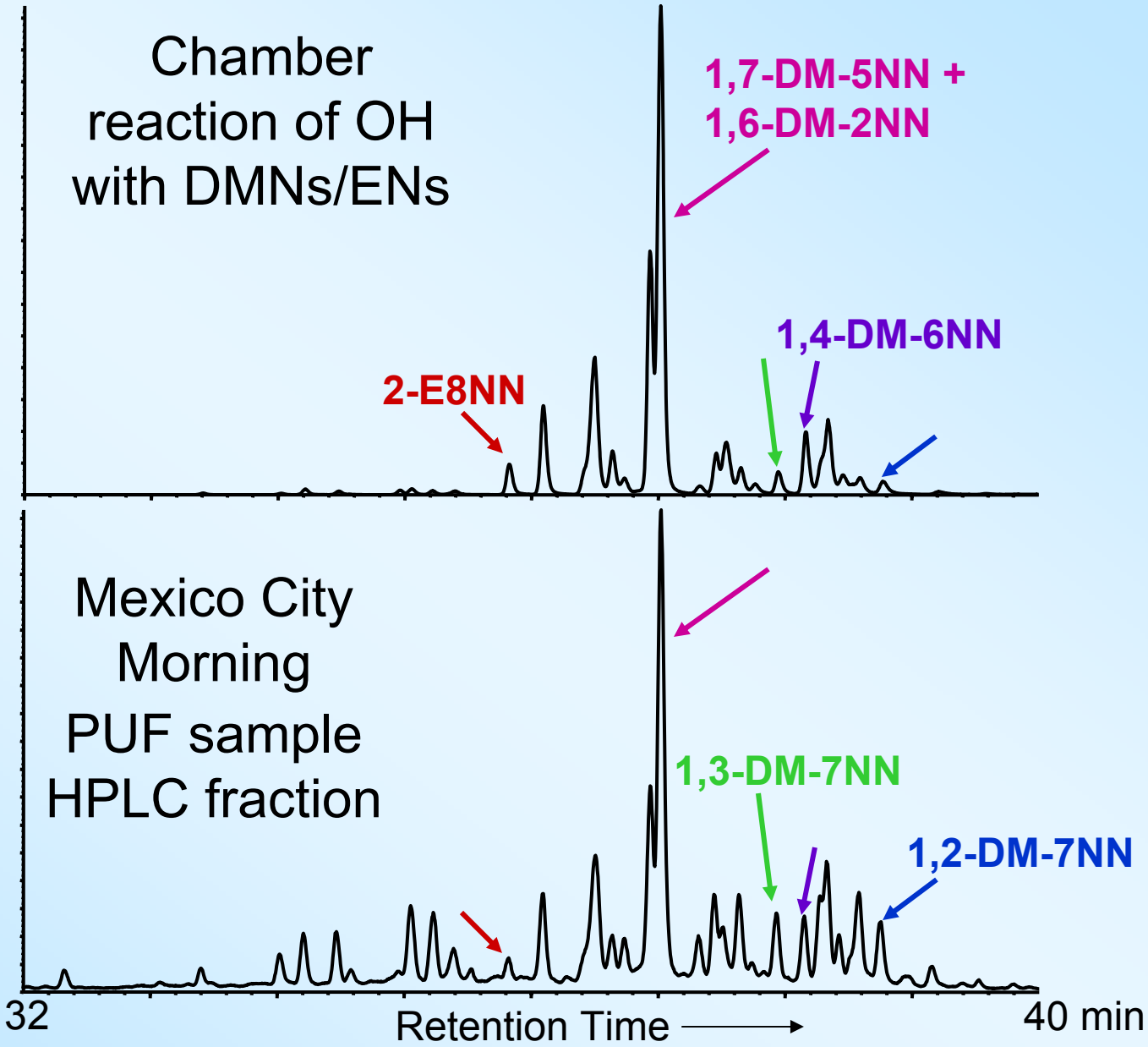


DMNNs/ENNS
GC/MS-NCI
m/z 201

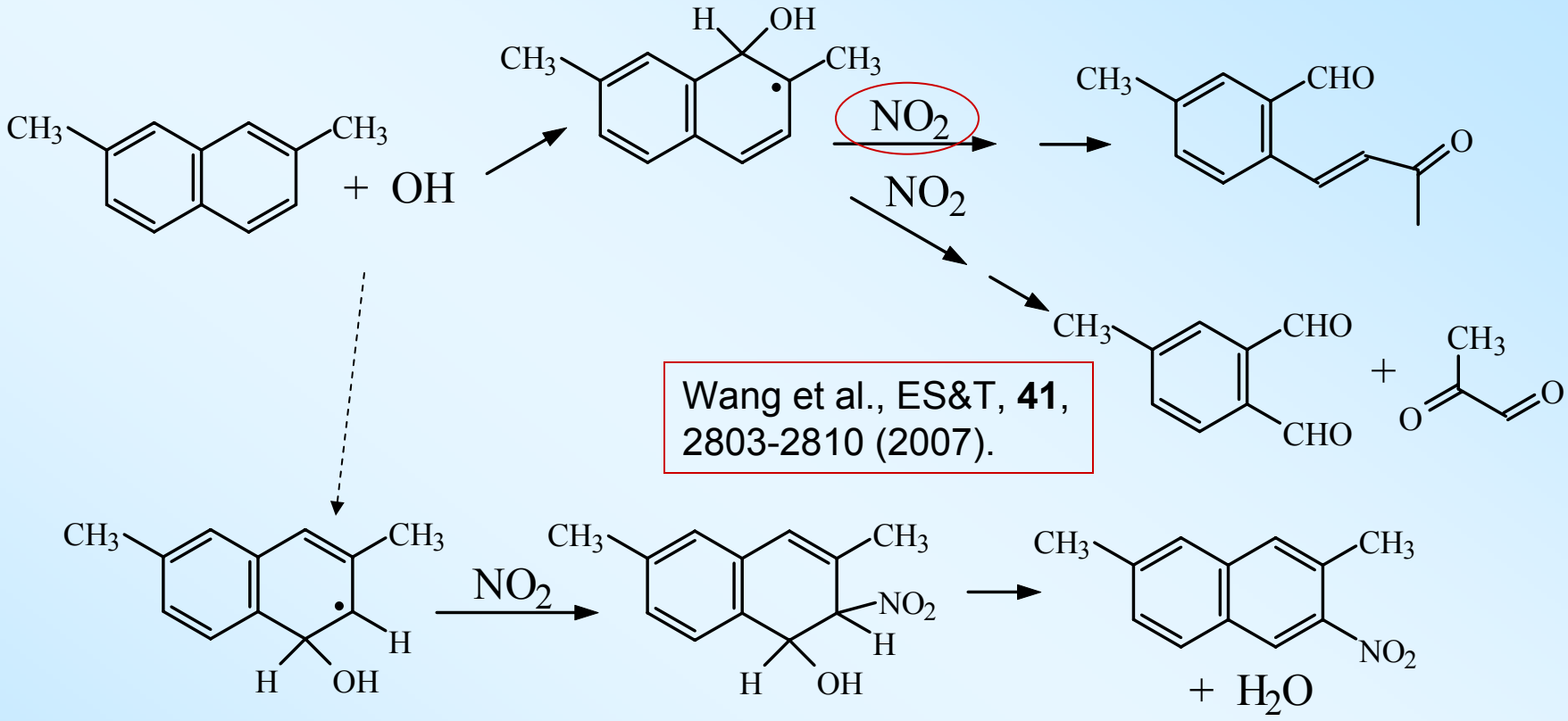
In the previously published reaction of "diesel DMNs/ENs" + OH, the early-eluting peaks were artifacts.

Some NO_3 chemistry in Mexico City??

or electrophilic nitration??



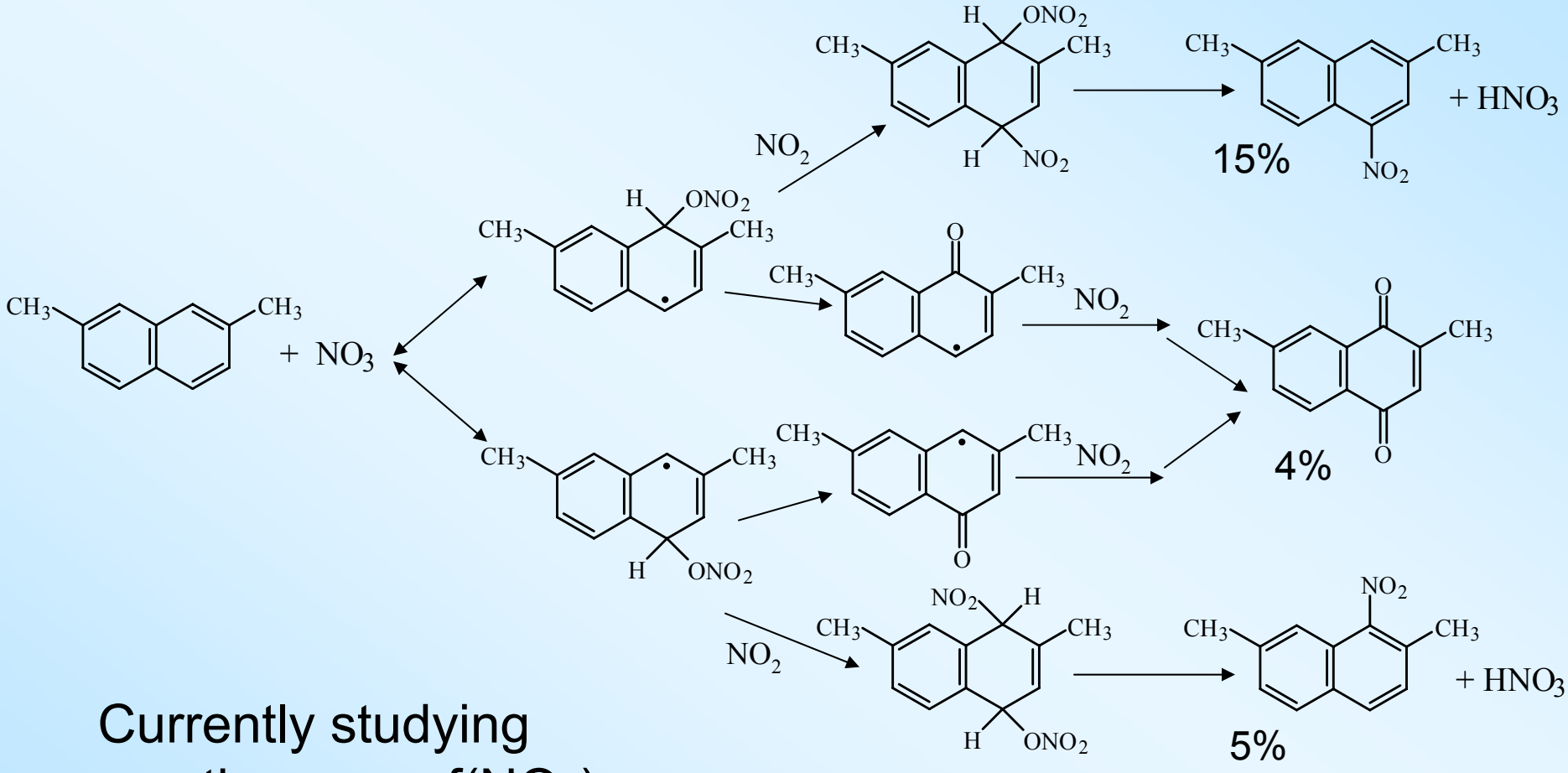
Yields of DMNNs/ENNs from OH radical reactions are small.



Products: ring-opened dialdehydes > dialdehydes with loss of 2-beta carbons (co-products, glyoxal, methylglyoxal and biacetyl) > dimethylnitronaphthalenes.

RA will discuss NO_2 dependence!

DMNNs/ENNs & quinones formed from NO_3 radical reactions.

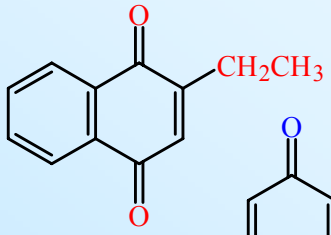


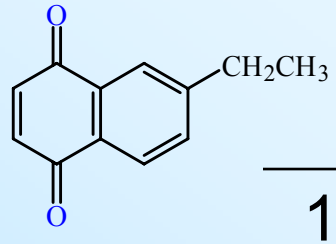
Currently studying reactions as a f(NO_2).

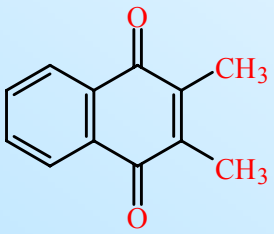
Yields shown are for 1ppm NO_2.

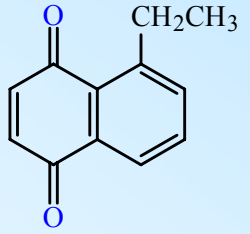
In NO_3 radical-initiated reactions, compounds with alkyl group(s) on β-carbon(s) form more quinones.

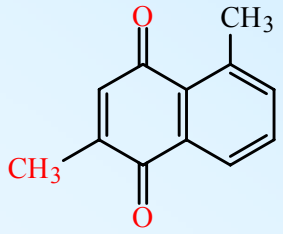
Compound	Quinone	Yield
1-MN	1-M-5,8-NQ	0.7
2-MN	2-M-1,4-NQ	3.4
	2-M-5,8-NQ	0.6
1-EN	1-E-5,8-NQ	0.3
2-EN	2-E-1,4-NQ	1.8
	2-E-5,8-NQ	0.4
1,6-DMN	1,6-DM-5,8-NQ	1.8
1,7-DMN	1,7-DM-5,8-NQ	0.8
2,3-DMN	2,3-DM-1,4-NQ	4.1
2,6-DMN	2,6-DM-1,4-NQ	2.2
2,7-DMN	2,7-DM-1,4-NQ	3.9

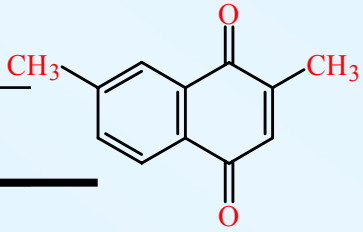




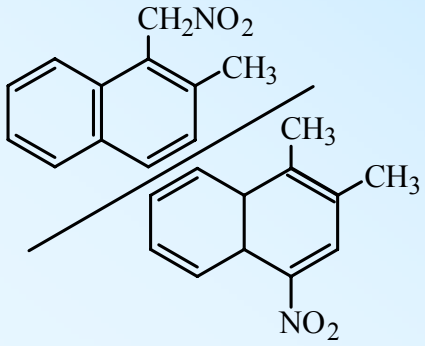


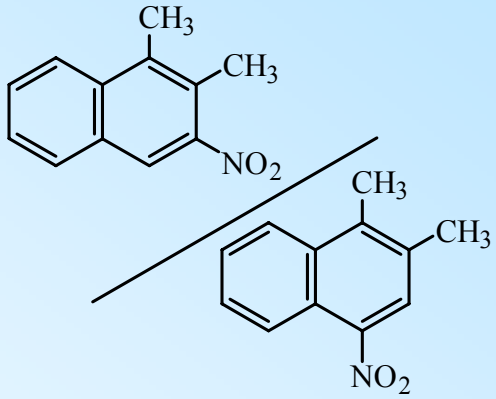






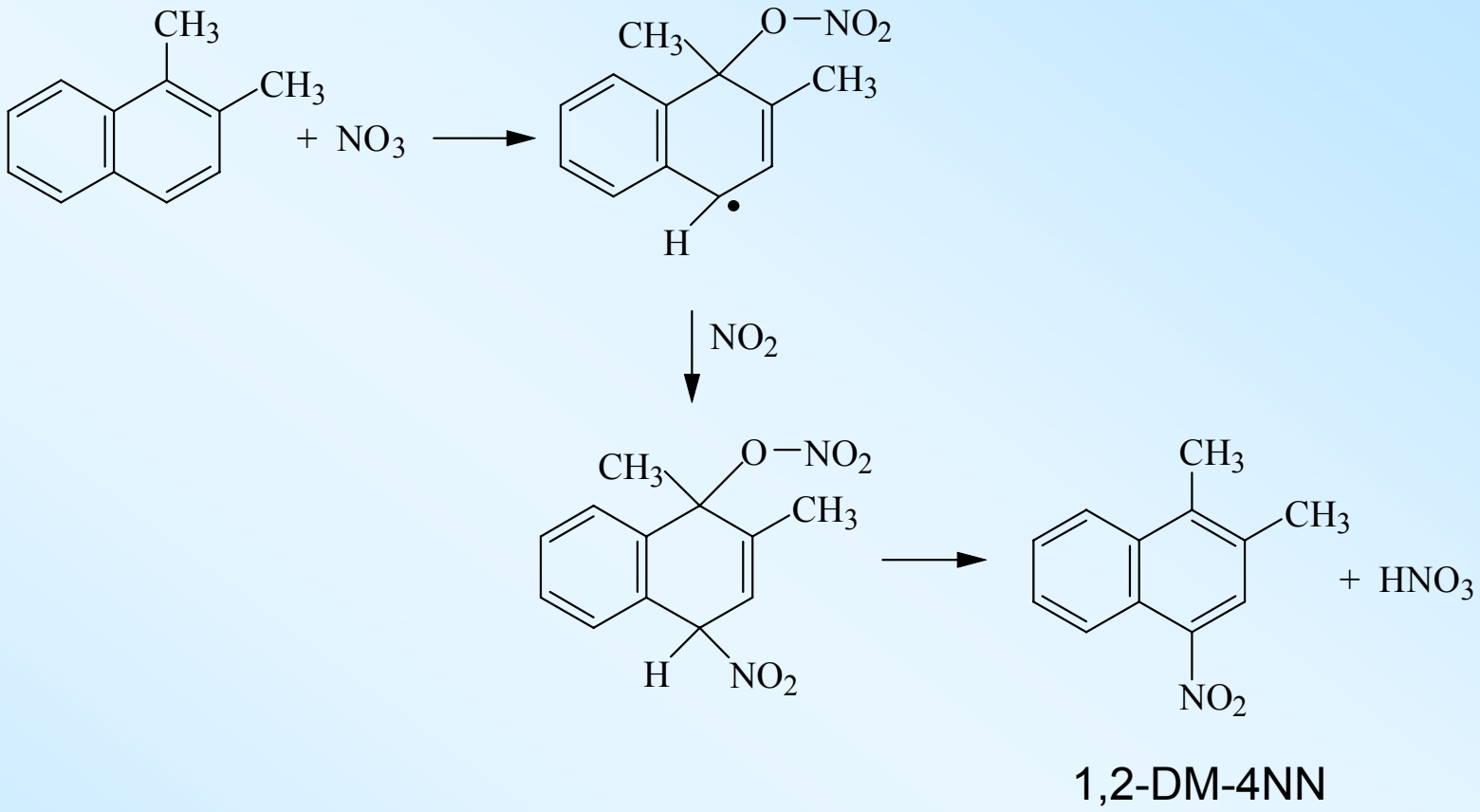
Nitration of the alkyl group was seen for 1,2-DMN, 1,4-DMN, 1,8-DMN and 1,3-DMN.





	side-chain 1,2-DM-4NN	1,2-DM-3NN 1,2-DM-4NN
MTC	0.3	0.05
ITC	0.01	0.04

The relative yield of the side-chain nitro-product/1,2-DM-4NN varies by a factor of 30 between the two chambers used. This suggests that the side-chain nitration is heterogeneous and the MTC may have had “wall problems”.



1,2-DM-4NN

Postulated mechanism of reaction of 1,2-DMN with the NO_3 radical showing *ipso* addition to give the major nitro-product, 1,2-DM-4NN.

Recommendations for Future Research

- Questions remain regarding mechanisms following the initial addition of the OH and NO_3 radicals to naphthalene and alkylnaphthalenes. The *ipso* addition of OH and/or NO_3 radicals with alkyl-PAH should be further investigated.

- The apparent NO_x dependence of the quinone yields from the photolysis of alkylnitronaphthalenes must be assessed.

- Ambient measurements of quinones should be made at upwind and downwind sites and locations where NO_3 radical chemistry is likely and unlikely to occur in order to evaluate the importance of atmospheric formation and confirm laboratory chamber data with ambient observations.

- Potential artifactual formation of DMNNs/ENNs during ambient sampling should be evaluated.

Papers resulting from this contract:

1. **Kinetics and Products of Photolysis and Reaction with OH Radicals of a Series of Aromatic Carbonyl Compounds.** (2006) Wang, L., J. Arey and R. Atkinson, Environ. Sci. Technol., 40, 5465-5471.

2. **Formation of 9,10-Phenanthrenequinone by Atmospheric Gas-phase Reactions of Phenanthrene.** (2007) Wang, L., R. Atkinson and J. Arey, Atmos. Environ., 41, 2025-2035.

3. **Dicarbonyl Products of the OH Radical-Initiated Reactions of Naphthalene and the C_1 and C_2-Alkylnaphthalenes.** (2007) Wang, L., R. Atkinson and J. Arey, Environ. Sci. Technol., 41, 2803-2810.

4. **Mechanisms of the Gas-Phase Reactions of Aromatic Hydrocarbons and PAHs with OH and NO_3 Radicals.** (2007) Atkinson, R. and J. Arey, Polycyclic Aromatic Compounds, 27, 15-40.

5. **Synthesis and Identification of Dimethylnitronaphthalenes and Ethylnitronaphthalenes to Aid in their Analysis in Ambient Air.** (2007) Gallagher, K.A. and J. Arey, Polycyclic Aromatic Compounds, 27, 211-237.